II. Variational methods in L^2

-) The Thomas-Fermi-von Weisäcker theory of atoms and molecules

-) Definition of the functional and some basic properties (Coercivity, continuity, and variational sets)

-) Existence of minimizers (precompactness of minimizing sequences, binding inequalities, Euler-Lagrange equation, Convexity)

-) Minimizers in the Coulomb case (Stability of neutral and positively charged atoms and molecules, regularity and exponential decay of minimizers)

1.) The Thomas-Fermi-von Weisäcker theory of atoms and molecules

Atoms and molecules are in quantum mechanics described by the time-dependent Schrödinger equation

$$\begin{cases} i\partial_t \Psi_t = H\Psi_t \\ \Psi_0 = \Psi \end{cases} \tag{1}$$

Here H denotes the Hamiltonian of the system and Ψ is the wave function, whose knowledge allows us to compute all the physical quantities we may be interested in. Associated with H is the energy functional

$$\mathcal{E}(\Psi) = \langle \Psi, H\Psi \rangle. \tag{2}$$

In the last section we learned that any minimizer of the problem $\inf\limits_{\|\Psi\|_2=1} \mathcal{E}(\Psi)$ solves the time-independent

Schrödinger equation

$$H\Psi = E\Psi \tag{3}$$

for some energy $E \in \mathbb{R}$. If a solution Ψ of (3) is chosen as initial condition in (1), then $\Psi_t = e^{-iEt}\Psi$ solves (1).

The lowest energy state of atoms and molecules is described by the minimizer of $\mathcal{E}$. To describe a systems with M atomic nuclei with masses $\{M_i\}_{i=1}^M$ and charges $\{Z_i\}_{i=1}^M$ and N electrons of mass m, we need to choose H (in suitable units) as

(1b) (2a)

$$H = \sum_{i=1}^{M} \frac{-\Delta_{y_i}}{2M_i} + \sum_{i=1}^{N} \frac{-\Delta_{x_i}}{2m} + \sum_{1\le i<j\le M} \frac{Z_i Z_j}{|y_i - y_j|}$$

(1a) (2b)

$$+ \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_j}{|x_i - y_j|}. \tag{4}$$

(3)

The terms in the Hamiltonian denote the

(1a/b) kinetic energy of the nuclei/electrons,

(2a/b) Coulomb repulsion between the nuclei/electrons,

(3) Coulomb attraction between the nuclei and the electrons.

It should be noted that $\mathcal{E}(\Psi)$ needs to be minimized over functions with $\|\Psi\| = 1$ and $\Psi \in H^1$ that satisfy additional constraints. We will come back to this in a moment.

Solving this minimization problem on a computer is possible only for very small values of N and M. This is due to the fact that the numerical complexity increases exponentially with the particle number, which is called the curse of dimensionality. To circumvent this problem physicists make approximations that are motivated by heuristic considerations. Since the results will later be compared to experiments this is a reasonable approach.

The first approximation is to fix the positions of the nuclei and to treat them as parameters. This is motivated by the fact that the M_i are at least by a factor 1000 larger than m (this is the case for $Z=1$). The kinetic energy of the nuclei can later be added again to the problem (Born-Oppenheimer approximation) but we will not discuss this issue here. The wave function of the resulting minimization problem only depends on the coordinates $x_1, \dots, x_N$. They appear in a symmetric way in the Hamiltonian because the masses of all electrons are the same. This symmetry of the Hamiltonian causes solutions of the Schrödinger equation to have one of two symmetries

(I skip a few details and subtleties here).

$$\Psi(x_1 \dots x_i \dots x_j \dots x_N) = \Psi(x_1 \dots x_j \dots x_i \dots x_N) \tag{5}$$

holds for all $1 \leq i < j \leq N$ or

$$\Psi(x_1 \dots x_i \dots x_j \dots x_N) = - \Psi(x_1 \dots x_j \dots x_i \dots x_N) \tag{6}$$

holds for all $1 \leq i < j \leq N$. Both mathematical possibilities occur in nature. Particles obeying (5) are called bosons and particles obeying (6) are called fermions. All elementary particles that we find in nature are either bosons or fermions. Electrons turn out to be fermions and so we need to minimize $\mathcal{E}$ over functions $\Psi \in \mathcal{H}^N$ with $\|\Psi\| = 1$ that obey (6). This is important because minimization over functions that obey (5) yields a lower minimal energy. The constraint in (6) is responsible for much of the complexity that we find in the world of atoms, molecules, and materials.

A function obeying (6) satisfies $\Psi(x_1 \ldots x_N) = 0$ if $x_i = x_j$ for a pair (i,j). This is the famous Pauli exclusion principle (two fermions are never allowed to do "the same thing").

Next, I would like to briefly discuss two inequalities that we will use to motivate the energy functional that we will study in the second part of the lecture.

<u>Theorem (Lieb–Thirring inequality)</u>: There exists a constant $C > 0$ (independent of N) such that

$$\left\langle \Psi, \left(\sum_{i=1}^{N} \frac{-\Delta_{x_i}}{2} \right) \Psi \right\rangle \geq C \int_{\mathbb{R}^3} \rho_\Psi(x)^{5/3} \, dx \qquad (7)$$

holds for any N-particle fermionic wave function $\Psi \in H^1((\mathbb{R}^3)^N)$ with $\int |\Psi(x_1, \ldots, x_N)|^2 \, d(x_1 \ldots x_N) = 1$.

Here $\rho_\Psi(x) = N \int |\Psi(x, x_2, \ldots, x_N)|^2 \, d(x_2, \ldots, x_N)$ denotes the

1-particle density of Ψ.

Theorem (Lieb-Oxford inequality): There exists a constant $C_D > 0$ (independent of N) such that

$$\left\langle \Psi, \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} \Psi \right\rangle \geq \frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho_\Psi(x)\,\rho_\Psi(y)}{|x-y|}\, d(x,y)$$

$$- C_D \int_{\mathbb{R}^3} \rho_\Psi(x)^{4/3}\, dx \qquad (8)$$

holds for any bosonic or fermionic wave function $\Psi \in H^1((\mathbb{R}^3)^N)$ with $\int |\Psi(x_1, \dots, x_N)|^2 d(x_1 \dots x_N) = 1$.

Let us apply these two inequalities to obtain a lower bound for the energy functional

$$\tilde{\mathcal{E}}(\Psi) = \langle \Psi, \tilde{H} \Psi \rangle, \qquad (9)$$

where $\tilde{H}$ denotes the Hamiltonian in (4) without the kinetic term of the nuclei and the repulsive interaction between them. We have

$$\tilde{H} = \sum_{i=1}^{N} \frac{-\Delta_{x_i}}{2m} + \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{Z_i}{|x_i - R_j|}, \tag{10}$$

where $\{R_j\}_{j=1}^{M}$ denote the positions of the nuclei and $\{Z_j\}_{j=1}^{M}$ their charges, as well as

$$\tilde{\mathcal{E}}(\Psi) \geq C_1 \int_{\mathbb{R}^3} \rho_\Psi(x)^{5/3}\,dx + \frac{1}{2}\int_{\mathbb{R}^6} \frac{\rho_\Psi(x)\rho_\Psi(y)}{|x-y|}\,d(x,y)$$

$$+ \int_{\mathbb{R}^3} \rho_\Psi(x)\,V_M(x)\,dx - C_D \int_{\mathbb{R}^3} \rho_\Psi^{4/3}(x)\,dx. \tag{11}$$

Here $V_M(x) = -\sum_{j=1}^{M} \frac{Z_j}{|x-R_j|}$ and we used the symmetry of the function Ψ to obtain the last term on the r.h.s. of (11).

The advantage of the r.h.s. of (11) is that it depends only on the density $\rho_\Psi(x)$ of Ψ. It is therefore much easier to study (mathematically and numerically). From practical experience we know that the quality of this approximation increases if a term of the form

$$\int |\nabla \sqrt{\rho_\Psi(x)}|^2 dx \tag{12}$$

is added to the problem. This can also be motivated by the following inequality.

<u>Theorem:</u> Let $\Psi \in H^1((\mathbb{R}^3)^N)$ be a bosonic or fermionic wave function with $\int |\Psi(x_1 \dots x_N)|^2 d(x_1 \dots x_N) = 1$. Then $\rho_\Psi \in H^1(\mathbb{R}^3)$ and we have the bound

$$\langle \Psi, \sum_{i=1}^N -\Delta_i \Psi \rangle \geq \int_{\mathbb{R}^3} |\nabla \sqrt{\rho_\Psi(x)}|^2 dx . \tag{13}$$

If we add the term in (12) to the r.h.s. of (11) we obtain the Thomas-Fermi-von Weisäcker-Dirac (TFWD) energy functional

$$\mathcal{F}(\rho) = \frac{3}{5} C_{TF} \int_{\mathbb{R}^3} \rho(x)^{5/3}\, dx + \frac{C_W}{2} \int_{\mathbb{R}^3} \left|\nabla \sqrt{\rho(x)}\right|^2 dx \qquad (14)$$

$$+ \frac{1}{2} \int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|}\, d(x,y) - \frac{3}{4} C_D \int_{\mathbb{R}^3} \rho(x)^{4/3}\, dx + \int_{\mathbb{R}^3} V_{\underline{u}}(x)\rho(x)\, dx,$$

which depends on the number of electrons N via the normalization condition

$$\int_{\mathbb{R}^3} \rho(x)\, dx = N. \qquad (15)$$

The functional $\mathcal{F}$ has been studied in great detail in the early days of atomic and molecular physics. For modern applications it is, however, too simple.

From a mathematical point of view it is a formidable model to learn techniques from the calculus of variations, which is our main goal.

2. Definition of the functional and some basic properties

It is convenient to use $\phi(x) = \sqrt{\rho(x)}$ as main variable because it naturally lives in the Hilbert space $H^1(\mathbb{R}^3)$. In contrast, $\rho \in L^1(\mathbb{R}^3)$, which is not a reflexive Banach space. This leads us to define the following energy functional

$$\mathcal{E}^V(\phi) = \frac{c_W}{2} \int_{\mathbb{R}^3} |\nabla \phi(x)|^2 dx + \frac{3}{5} c_{TF} \int_{\mathbb{R}^3} |\phi(x)|^{10/3} dx \qquad (16)$$

$$+ \int_{\mathbb{R}^3} V(x) |\phi(x)|^2 dx + \frac{1}{2} \int_{\mathbb{R}^6} \frac{|\phi(x)|^2 |\phi(y)|^2}{|x-y|} d(x,y).$$

Note that we neglected the negative term in (14). This is because it requires more advanced techniques than those that we will introduce in the following. The functional $\mathcal{E}^V$ is called Thomas-Fermi-von Weizsäcker (TFW) functional. The external potential V is given by

$$V(x) = -\sum_{m=1}^{M} \frac{Z_m}{|x - R_m|} \,. \tag{17}$$

By $Z = \sum_{m=1}^{M} Z_i$ we denote the total nuclear charge. A-priori ϕ is a nonnegative function but it is convenient to allow for complex-valued ϕ. For the sake of simplicity we will also set $c_W = 1$. It should also be noted that $c_{TF} > 0$.

The first step in our investigation of $\mathcal{E}^V$ is to show that it is well-defined on $H^1(\mathbb{R}^3)$.

Lemma 1: The functional $\mathcal{E}^V$ is well-defined and continuous on $H^1(\mathbb{R}^3)$.

Proof: Let $\phi \in H^1(\mathbb{R}^3)$. We would like to show that each term in the definition of $\mathcal{E}^V(\phi)$ is finite. The first term is trivially finite. To show that the second term is finite we note that

$$\|\phi\|_{10/3} \leq \|\phi\|_2^{\Theta} \, \|\phi\|_6^{1-\Theta} \tag{18}$$

$$\lesssim \|\phi\|_2^{\Theta} \, \|\nabla\phi\|_2^{1-\Theta}$$

Sobolev inequality

$$\boxed{a \lesssim b \iff \exists\, C>0 \text{ s.t. } a \leq Cb. \quad \text{(Def.)}}$$

holds for $\Theta = 2/5$.

$$\boxed{\begin{aligned} &\frac{3}{10} = \frac{\Theta}{2} + \frac{1-\Theta}{6} \\ \iff\; &\underbrace{\frac{3}{10} - \frac{1}{6}}_{\frac{4}{30}} = \Theta \underbrace{\left(\frac{1}{2} - \frac{1}{6}\right)}_{\frac{1}{3}} \\ \iff\; &\Theta = \frac{12}{30} = \frac{2}{5} \end{aligned}}$$

Next, we choose $r>0$ and note that

$$\int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x-R|}\,dx = \overbrace{\int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x-R|} \mathbb{1}(|x-R| \leq r)\,dx}^{ⓐ}$$

$$+ \overbrace{\int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x-R|} \mathbb{1}(|x-R| > r)\,dx}^{ⓑ}. \tag{19}$$

We have

$$\boxdot \quad ⓐ \underset{\substack{\uparrow \\ \text{Hölder}}}{\leq} \underbrace{\|\phi\|_6^2}_{\lesssim \|\nabla\phi\|_2^2} \Bigg(\underbrace{\int_{\mathbb{R}^3} \frac{1}{|x-R|^{3/2}} \mathbb{1}(|x-R| \leq r)\, dx}_{= 4\pi \int_0^r \frac{1}{y^{3/2}} y^2\, dy = \frac{8\pi}{3} r^{3/2}} \Bigg)^{2/3}$$

$$\lesssim \|\nabla\phi\|_2^2 \, r, \tag{20}$$

$$\boxdot \quad ⓑ \leq \frac{1}{r} \|\phi\|_2^2 . \tag{21}$$

In combination, (19), (20), and (21) show the existence of (an explicit) constant $C>0$ s.t.

$$\int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x-R|}\, dx \leq \frac{\|\phi\|_2^2}{r} + Cr \|\nabla\phi\|_2^2 . \tag{22}$$

This shows that the third term on the r.h.s. of (16) is finite. Using (22), we also see that the fourth term is finite because

$$\int_{\mathbb{R}^6} \frac{|\phi(x)|^2 |\phi(y)|^2}{|x-y|} d(x,y) \leq \int_{\mathbb{R}^3} |\phi(y)|^2 \left(\frac{\|\phi\|_2^2}{r} + C_r \|\nabla\phi\|_2^2 \right) dy$$

$$= \|\phi\|_2^2 \left(\frac{\|\phi\|_2^2}{r} + C_r \|\nabla\phi\|_2^2 \right). \qquad (23)$$

This proves that $\mathcal{E}^V$ is well-defined on $H^1(\mathbb{R}^3)$. The continuity of $\mathcal{E}^V$ on $H^1(\mathbb{R}^3)$ is left as an exercise.

Exercise 1: Show that the map $\phi \mapsto \mathcal{E}^V(\phi)$ is continuous on $H^1(\mathbb{R}^3)$.

This proves Lemma 2.1. $\blacksquare$

Remark 1: By paying more attention to constants than we did, one can prove that

$$\int_{\mathbb{R}^3} \frac{|\phi(x)|^2}{|x-R|} \leq \eta \int_{\mathbb{R}^3} |\nabla\phi(x)|^2 dx + \frac{1}{4\eta} \int_{\mathbb{R}^3} |\phi(x)|^2 dx \qquad (24)$$

holds for $\phi \in H^1(\mathbb{R}^3)$ and any $\eta > 0$, which is known as **Kato's inequality.**

Recall that $\int \rho(x)\,dx$ equals the number of electrons in the system. We are interested in the following minimization problem

$$J^V(\lambda) = \inf_{\substack{\phi\in H^1(\mathbb{R}^3) \\ \int|\phi|^2 dx = \lambda \\ \phi \geq 0}} \mathcal{E}^V(\phi). \qquad (25)$$

Before we investigate this problem in more detail, we argue that the constraint $\phi \geq 0$ can be dropped. We have

$$\inf_{\substack{\phi\in H^1(\mathbb{R}^3) \\ \int|\phi|^2 dx = \lambda \\ \phi \geq 0}} \mathcal{E}^V(\phi) \geq \inf_{\substack{\phi\in H^1(\mathbb{R}^3) \\ \int|\phi|^2 dx = \lambda}} \mathcal{E}^V(\phi) \qquad (26)$$

because we minimize over a larger set on the r.h.s..

The reverse inequality is obtain with the convexity inequality for gradients

$$\int_{\mathbb{R}^3} \big| \nabla |\phi(x)| \big|^2 dx \leq \int_{\mathbb{R}^3} |\nabla \phi(x)|^2 dx \tag{27}$$

that we proved in the first part of the lecture. We thus have

$$\mathcal{E}^V(|\phi|) \leq \mathcal{E}^V(\phi). \tag{28}$$

In combination with (26), this proves

$$\inf_{\substack{\phi \in H^1(\mathbb{R}^3) \\ \int |\phi|^2 dx = \lambda \\ \phi \geq 0}} \mathcal{E}^V(\phi) = \inf_{\substack{\phi \in H^1(\mathbb{R}^3) \\ \int |\phi|^2 dx = \lambda}} \mathcal{E}^V(\phi). \tag{29}$$

In particular, we do not have to worry about the constraint $\phi \geq 0$.

Our goal is to show that the minimization problem

$$\boxed{J^{\nu}(\lambda) = \inf_{\substack{\phi \in H^1(\mathbb{R}^3) \\ \int |\phi|^2 dx = \lambda}} \mathcal{E}^{\nu}(\phi)} \tag{30}$$

admits a minimizer, that is, we want to show that there exists $\tilde{\phi} \in H^1(\mathbb{R}^3)$ with $\int |\tilde{\phi}(x)|^2 dx = \lambda$ and $\mathcal{E}^{\nu}(\tilde{\phi}) = J^{\nu}(\lambda)$.

To be sure that this is a well-posed question we first have to check that $\mathcal{E}^{\nu}$ is bounded from below! This is guaranteed by the following lemma.

Lemma 2: Recall the definition of Z on p.12. The inequality

$$\mathcal{E}^V(\phi) \geq \frac{1}{4} \|\nabla \phi\|_2^2 - Z^2 \|\phi\|_2^2 \qquad (31)$$

holds for all $\phi \in H^1(\mathbb{R}^3)$.

Proof: We have

$$\mathcal{E}^V(\phi) \geq \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi(x)|^2 dx + \int_{\mathbb{R}^3} V(x) \, |\phi(x)|^2 dx. \qquad (32)$$

Next, we apply Kato's inequality in (24) to each term in the definition of V in (17) separately and find

$$- \int_{\mathbb{R}^3} V(x) \, |\phi(x)|^2 dx \leq Z\eta \int_{\mathbb{R}^3} |\nabla \phi(x)|^2 + \frac{Z}{4\eta} \int_{\mathbb{R}^3} |\phi(x)|^2 dx, \qquad (33)$$

where we used $\sum_{m=1}^{M} z_m = Z$. We combine (32) and (33) with the choice $\eta = \frac{1}{4Z}$, and find the lower bound

$$\mathcal{E}^V(\phi) \geq \frac{1}{4} \int_{\mathbb{R}^3} |\nabla\phi(x)|^2\, dx - Z^2 \int_{\mathbb{R}^3} |\phi(x)|^2 dx. \tag{34}$$

$\blacksquare$

From Lemma 2 we learn (a) that $\mathcal{E}^V$ is bd. from below and (b) that $H^1(\mathbb{R}^3)$ is the natural domain of $\mathcal{E}^V$. In all our considerations $\int |\phi(x)|^2 dx$ will be fixed (or at least bounded). If there is a sequence with $\int |\nabla\phi_n(x)|^2 dx \to +\infty$ then $\mathcal{E}^V(\phi_n) \to +\infty$. This property is called coercivity.

We say that $\mathcal{E}^V$ is coercive on $H^1(\mathbb{R}^3)$.

If you are unsure about the question what the natural domain of a functional is, then you should prove a lower bound and see on which set the functional is coercive. If you can also prove an upper bound for functions in this set then you have found its natural domain.

Discussion of the minimization problem: Assume we are given a minimizing sequence $\{\phi_n\}_{n=1}^{\infty}$ for $\mathcal{E}^V$. From Lemma 2 and the constraint $\int |\phi(x)|^2 dx = \lambda$ we know that its $H^1(\mathbb{R}^3)$-norm is uniformly bounded. That is, it has a weakly convergent (in H^1) subsequence. Unfortunately the set

$$S(\lambda) := \left\{ \phi \in H^1(\mathbb{R}^3) \;\middle|\; \int |\phi(x)|^2 dx = \lambda \right\} \tag{35}$$

is not closed in the weak topology of $H^1(\mathbb{R}^3)$ as the following example shows:

Choose $\varphi, \psi \in C_c^\infty(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} |\varphi(x)|^2 dx = 1 = \int_{\mathbb{R}^3} |\psi(x)|^2 dx$.

Define the sequence $\varphi_n(x) = \sqrt{\lambda'}\,\varphi(x) + \sqrt{\lambda - \lambda'}\,\psi(x - nv)$, where $v \in \mathbb{R}^3$, $v \neq 0$ and $0 \leq \lambda' \leq \lambda$.

stays at one point

escapes to infinity for $n \to \infty$

For n large enough we have

$$\int_{\mathbb{R}^3} |\varphi_n(x)|^2 dx = \lambda' \int_{\mathbb{R}^3} |\varphi(x)|^2 dx + (\lambda-\lambda') \int_{\mathbb{R}^3} |\psi(x)|^2 dx = \lambda , \qquad (36)$$

that is, $\varphi_n \in S(\lambda)$ for n large enough. On the other hand, one easily checks that $\varphi_n \xrightarrow{n\to\infty} \lambda' \varphi$ in $H^1(\mathbb{R}^3)$.

Exercise 2: Prove this claim.

Therefore we can have a weak limit, which has any mass $0 \le \lambda' \le \lambda$. In particular, $S(\lambda)$ is not closed in the weak topology of $H^1(\mathbb{R}^3)$.

The fact that minimizing sequences can have a part, which escapes to infinity is the main "disease" that we have to face in this study. One says that the problem has a lack of compactness at infinity.

This mathematical phenomenon is related to an obvious physical phenomenon. Since atomic nuclei in nature cannot bind an arbitrary number of electrons we expect the same to be true for our model!

In general, the possible limits of weakly convergent sequences $\phi_n \rightharpoonup \phi$ in $H^1(\mathbb{R}^3)$ belong to the convex hull of $S(\lambda)$, which is nothing but

$$S_{\leq}(\lambda) = \left\{ \phi \in H^1(\mathbb{R}^3) \;\middle|\; \int |\phi(x)|^2 dx \leq \lambda \right\}. \qquad (37)$$

Following the example from above it is not difficult to show that any $\phi \in S_{\leq}(\lambda)$ is the weak limit of a sequence $\{\phi_n\}_{n=1}^{\infty}$ with $\phi_n \in S(\lambda)$. Finally, when $\phi_n \rightharpoonup \phi$ in $H^1(\mathbb{R}^3)$, then $\phi_n \rightharpoonup \phi$ in $L^2(\mathbb{R}^3)$. But we know from the first part of the lecture that the

$L^2(\mathbb{R}^3)$-norm is weakly lower semicontinuous, that is,

$$\liminf_{n\to\infty} \int_{\mathbb{R}^3} |\phi_n(x)|^2 dx \geq \int_{\mathbb{R}^3} |\phi(x)|^2 dx . \tag{38}$$

We conclude that a weak limit cannot have an L^2-norm larger than λ. Hence, $S_{\leq}(\lambda)$ is the closure of $S(\lambda)$ w.r.t. the weak topology of $H^1(\mathbb{R}^3)$ and that $S_{\leq}(\lambda)$ is closed in the same topology.

Since it will turn out to be useful later, we introduce also the following relaxed minimization problem

$$\boxed{J^V_{\leq}(\lambda) = \inf_{\substack{\phi\in H^1(\mathbb{R}^3) \\ \int|\phi|^2dx \leq \lambda}} \mathcal{E}^V(\phi)} . \tag{39}$$

Note that $S(\lambda) \subset S_{\leq}(\lambda)$ implies $J^V_{\leq}(\lambda) \leq J^V(\lambda)$.

Let us summarize our findings in the following Lemma:

Lemma 3: The set $S(\lambda)$ is closed in the strong topology of $H^1(\mathbb{R}^3)$ but not in the weak topology. Its convex hull $S_\leq(\lambda)$ is closed in the weak and in the strong topology of $H^1(\mathbb{R}^3)$. The set $S_\leq(\lambda)$ is the closure of $S(\lambda)$ in the weak topology of $H^1(\mathbb{R}^3)$.

3. Existence of minimizers

In this section we will prove the existence of minimizers for $J(\lambda)$ and for $J_{\leq}(\lambda)$. The result will depend on λ and is captured in the following theorem.

Theorem 1: There exists a $0 \leq \lambda_c \leq \infty$ s.t. the following holds.

(a) The function $\lambda \mapsto J^V(\lambda)$ is decreasing on the interval $[0, \lambda_c]$ and we have for $\lambda \in [0, \lambda_c]$:

(1) $J^V(\lambda)$ admits a unique minimizer $\phi_\lambda \geq 0$.

(2) $\phi_\lambda \in H^2(\mathbb{R}^3)$ and $\phi_\lambda(x) > 0$ holds for all $x \in \mathbb{R}^3$.

(3) ϕ_λ solves the nonlinear Schrödinger equation

$$\left(-\frac{\Delta}{2} + V + c_{TF}\,|\phi_\lambda|^{4/3} + |\phi_\lambda|^2 * \frac{1}{|x|}\right)\phi_\lambda = \mu_\lambda \phi_\lambda, \quad (40)$$

where the Lagrange multiplier $\lambda \in \mathbb{R}$ satisfies

$$\begin{aligned} \mu < 0 \quad &\text{for } 0 \leq \lambda < \lambda_c, \\ \mu = 0 \quad &\text{for } \lambda = \lambda_c. \end{aligned} \tag{41}$$

Moreover, μ is the lowest eigenvalue of the Schrödinger operator

$$H_{\phi_\lambda} = -\frac{\Delta}{2} + V + C_{TF} \, |\phi_\lambda|^{4/3} + |\phi_\lambda|^2 * \frac{1}{|x|}. \tag{42}$$

(4) All other minimizers for $J^V(\lambda)$ are of the form $z\phi_\lambda$ for a constant $z \in \mathbb{C}$ with $|z| = 1$. One says that ϕ_λ is unique up to a phase.

(5) The function ϕ_λ is (up to a phase factor) also the unique minimizer of $J_{\leq}(\lambda)$.

(6) All the minimizing sequences $\{\phi_n\}_{n=1}^{\infty}$ for $J^V(\lambda)$ are precompact in the strong topology of $H^1(\mathbb{R}^3)$

(here precompact means that the closure of the set is compact), that is, we have $\phi_{n_k} \to z\phi_\lambda$ strongly in $H^1(\mathbb{R}^3)$ for a subsequence and a constant $|z|=1$. If $\phi_n \geq 0$ for all n, then $\phi_n \to \phi_\lambda$ strongly in $H^1(\mathbb{R}^3)$. The same holds for minimizing sequences of $J^V_{\leq}(\lambda)$.

(7) The map $\lambda \mapsto J^V(\lambda)$ is continuously differentiable on $[0, \lambda_c]$ and we have $(J^V)'(\lambda) = \mu_\lambda$.

(b) The function $\lambda \mapsto J^V(\lambda)$ is constant on the interval $[\lambda_c, \infty)$ and we have for $\lambda > \lambda_c$:

(1) There is no minimizer for $J^V(\lambda)$.

(2) $J^V_{\leq}(\lambda)$ admits ϕ_{λ_c} as unique minimizer (up to a phase).

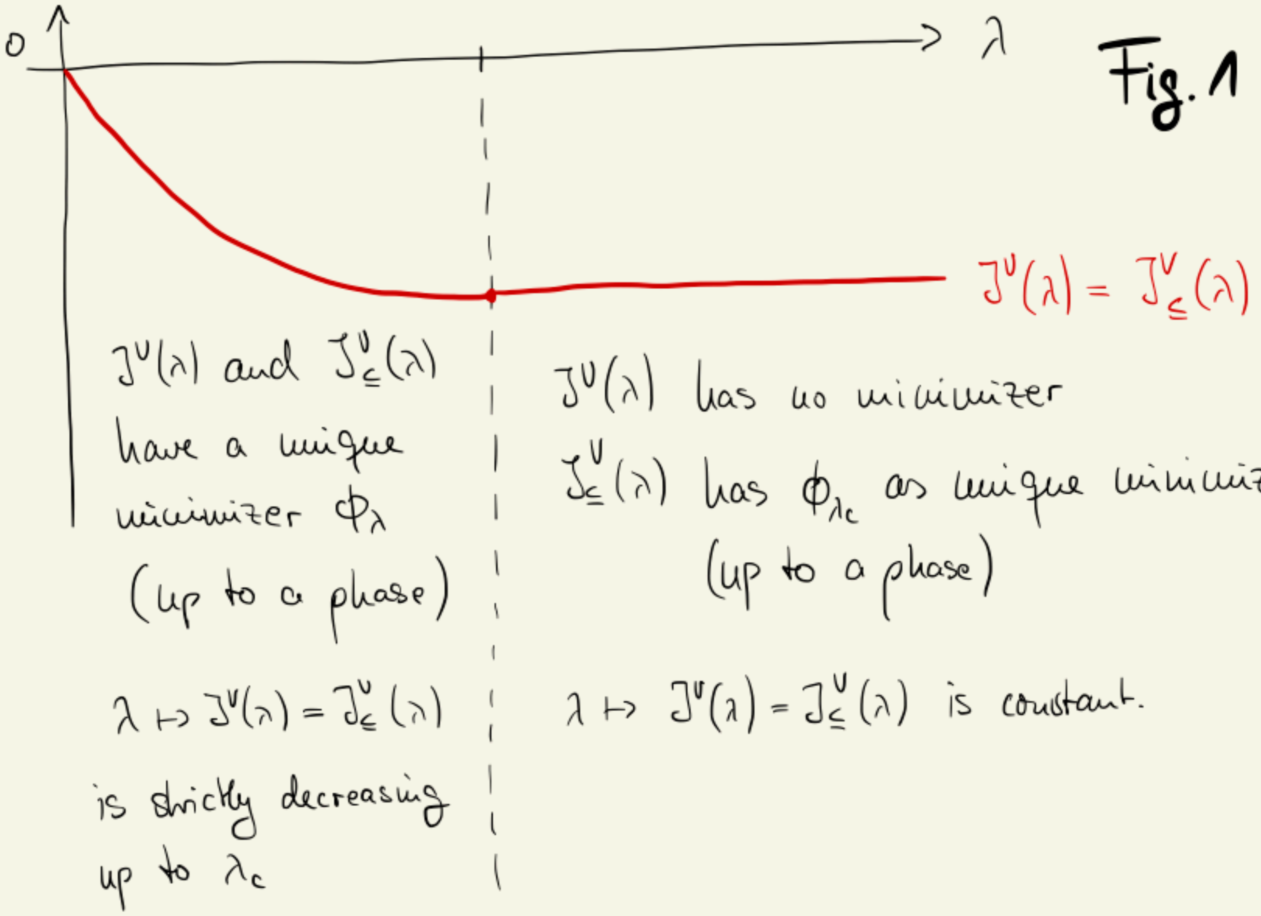
(3) If $\{\phi_n\}_{n=1}^{\infty}$ is a minimizing sequence for $J^V(\lambda)$

with $\Phi_n \geq 0$ for all n, then we have $\Phi_n \rightharpoonup \Phi_{\lambda_c}$ weakly in $H^1(\mathbb{R}^3)$. The same holds for minimizing sequences of $J^V_{\leq}(\lambda)$.

The number λ_c is interpreted as the maximal number of electrons that the potential V can bind. We will later prove the bound $Z \leq \lambda_c \leq 2Z$.

Remark 2: The theorem above shows that if V cannot bind λ electrons, then it can also not bind more electrons. It is a famous open problem to prove this statement, which seems to be natural, in the case of a description of the system with the Hamiltonian H in (4).

Fig. 1



The proof of Theorem 1 is not very difficult but long. We will organize it according to the following steps:

Step 1: Show that $\mathcal{E}^V$ is weakly lower semicontinuous in $H^1(\mathbb{R}^3)$ and deduce that $J^V_{\leq}(\lambda)$ has always at least one minimizer.

Step 2: Prove that $\lambda \mapsto J^V(\lambda)$ is non-increasing and has some other elementary properties.

Step 3: Prove of a criterion of precompactness for al minimizing sequences in terms of binding inequalities.

Step 4: Show that any minimizer ϕ_λ is a solution to the nonlinear Schrödinger equation in (40) with $\mu \le 0$. Use this to deduce that there is a $z \in \mathbb{C}$ with $|z|=1$ s.t. $z\phi_\lambda > 0$ and that μ is the lowest eigenvalue of H_{ϕ_λ} in (42).

Step 5. Proof of some convexity properties of $\mathcal{E}^V$ that are later used to show that $\lambda \mapsto J^V(\lambda)$ is convex. This will allow us to define λ_c and, using the previous results, we also get most of the statements of Theorem 1.

Step 6: Proof of some additional properties of μ. In particular, $\mu_\lambda < 0$ when $0 \le \lambda < \lambda_c$ and $\mu_{\lambda_c} = 0$. We will also show that $\mu_\lambda = (J^V)'(\lambda)$.

Step 1: Weak lower semi-continuity of $\mathcal{E}^V$ and consequences

We will first prove the following lemma.

Lemma 4 (wlsc of $\mathcal{E}^V$): The functional $\mathcal{E}^V$ is wlsc on $H^1(\mathbb{R}^3)$, that is, for every sequence $\{\phi_n\}_{n=1}^{\infty}$ with $\phi_n \rightharpoonup \phi$ weakly in $H^1(\mathbb{R}^3)$, we have

$$\mathcal{E}^V(\phi) \leq \liminf_{n\to\infty} \mathcal{E}^V(\phi_n). \tag{43}$$

Proof: From our analysis of the Schrödinger equation we know that the map $\phi \mapsto \int_{\mathbb{R}^3} V(x)\,|\phi(x)|^2\,dx$ is weakly continuous on $H^1(\mathbb{R}^3)$. Moreover, we have seen that the map $\phi \mapsto \int_{\mathbb{R}^3} |\nabla\phi(x)|^2\,dx$ is wlsc on $H^1(\mathbb{R}^3)$.

To treat the two remaining terms in the functional, we assume that $\phi_{n_k} \in H^1(\mathbb{R}^3)$ for $k \in \mathbb{N}$ with $\phi_{n_k} \rightharpoonup \phi \in H^1(\mathbb{R}^3)$ is a subsequence, for which $\lim_{k\to\infty} \mathcal{E}^V(\phi_{n_k}) = \liminf_{n\to\infty} \mathcal{E}^V(\phi_n)$ holds. From the Rellich-Kondrachov theorem we know that $\phi_{n_k} \to \phi$ in $L^p_{loc}(\mathbb{R}^3)$ for all $2 \leq p < 6$. Using this (see also the text in the brackets below) and a Cantor diagonal argument we see that there exists another subsequence that we continue to denote by the same symbol that converges p.w. a.e. to ϕ.

Exercise 3: Prove this statement.

[Here we used the following statement that you probably discussed in your analysis course:

Assume that $\Omega \subseteq \mathbb{R}^d$ and that $\{f^j\}_{j=1}^{\infty}$ is a sequence in $L^p(\Omega)$ with $1 \leq p \leq \infty$ and $f^j \to f$ strongly in $L^p(\Omega)$. Then there exists a subsequence f^{j_k} and a nonnegative function $F \in L^p(\Omega)$ s.t.

(a) Domination: $|f^{j_k}(x)| \le F(x)$ for all k and a.e. x.

(b) Pointwise convergence: $\lim_{k\to\infty} f^{j_k}(x) = f(x)$ for a.e. x.

Using the pointwise a.e. convergence and Fatou's lemma, we see that

$$\lim_{k\to\infty}\left(\int_{\mathbb{R}^3} |\phi_{n_k}(x)|^{10/3}\,dx + \int_{\mathbb{R}^6} \frac{|\phi_{n_k}(x)|^2\,|\phi_{n_k}(y)|^2}{|x-y|}\,d(x,y)\right)$$

$$\geq \int_{\mathbb{R}^3} |\phi(x)|^{10/3}\,dx + \int_{\mathbb{R}^6} \frac{|\phi(x)|^2\,|\phi(y)|^2}{|x-y|}\,d(x,y) \tag{45}$$

holds. This proves the claim of the lemma.

$\blacksquare$

Let us discuss some immediate consequences of Lemma 4.

Corollary 1 (Existence of a minimizer for the relaxed problem): For all $\lambda \geq 0$ there exists a minimizer of the relaxed problem $J^V_{\leq}(\lambda)$, that is, a function $\phi \in S_{\leq}(\lambda)$ with $\mathcal{E}^V(\phi) = J^V_{\leq}(\lambda)$. This minimizer can be chosen nonnegative.

Proof: Let $\{\phi_n\}_{n=1}^{\infty}$ be a minimizing sequence for $J^V_{\leq}(\lambda)$, that is, $\mathcal{E}^V(\phi_n) \to J^V_{\leq}(\lambda)$ holds for $n \to \infty$. The sequence $\mathcal{E}^V(\phi_n)$ is bounded and we conclude from the coercivity of $\mathcal{E}^V$ (see Lemma 2) that $\|\phi_n\|_{H^1(\mathbb{R}^3)}$ is uniformly bounded. This allows us to extract a subsequence ϕ_{n_k} and a function $\phi \in H^1(\mathbb{R}^3)$ s.t. $\phi_n \rightharpoonup \phi$ weakly in $H^1(\mathbb{R}^3)$. Since $S_{\leq}(\lambda)$ is closed in the weak topology of $H^1(\mathbb{R}^3)$, see Lemma 3, we know that $\phi \in S_{\leq}(\lambda)$. By the w.l.s.c. of $\mathcal{E}^V$ in Lemma 4 we have

$$J_{\leq}^{V}(\lambda) = \lim_{n\to\infty} \mathcal{E}^{V}(\phi_n) = \liminf_{k\to\infty} \mathcal{E}^{V}(\phi_{n_k}) \geq \mathcal{E}^{V}(\phi). \quad (46)$$

We conclude that $J_{\leq}^{V}(\lambda) = \mathcal{E}^{V}(\phi)$ and the existence of a minimizer for $J_{\leq}^{V}(\lambda)$ is proved.

From (28) we know that $\mathcal{E}^{V}(\phi) \geq \mathcal{E}^{V}(|\phi|)$. Hence if ϕ is a minimizer then $|\phi|$ is also a minimizer. Accordingly, we have shown that a nonnegative minimizer exists. This proves the claim. $\blacksquare$

Remark 3: If $\mathbb{R}^3$ is replaced by a bounded open set $\Omega \subset \mathbb{R}^3$, then $S(\lambda)$ is closed for the weak topology of $H^1(\mathbb{R}^3)$. Following the above proof we see that $J^V(\lambda)$ has a minimizer. It is only because of the lack of compactness at infinity that there is not always a minimizer when the problem is considered on the whole space. One says that the problem is **locally compact**.

Exercise 4: Show that $S(\lambda)$ is closed for the weak topology of $H^1_0(\Omega)$ when $\Omega\subset\mathbb{R}^3$ is a bounded open set.

Exercise 5: Replace $\mathbb{R}^3$ by a bounded open set $\Omega\subset\mathbb{R}^3$ and $H^1(\mathbb{R}^3)$ by $H^1_0(\Omega)$. Prove that $J^U(\lambda)$ has a minimizer for all $\lambda\geq 0$.

Exercise 6: Let X be a reflexive Banach space and let the set $S\subset X$ be closed in the weak topology of X. Moreover, let $\mathcal{E}: S\to\mathbb{R}$ be a functional that is bounded from below, w.l.s.c., and coercive on S.

Show that $\mathcal{E}$ always attains its infimum on S. Follow the strategy of the proof of Corollary 1 above.

Step 2: Basic properties of the function $\lambda \mapsto J^V(\lambda)$

The goal of this section is to prove the following lemma.

Lemma 5 (Basic properties of $J^V(\lambda)$): We have the following statements:

(a) The function $\lambda \mapsto J^V(\lambda)$ is continuous on $[0,\infty)$.

(b) One has $J^0(\lambda) = 0$ for all $\lambda \geq 0$.

(c) The function $\lambda \mapsto J^V(\lambda)$ is nonincreasing:

$$\forall \; 0 \leq \lambda' \leq \lambda \quad \text{we have } J^V(\lambda) \leq J^V(\lambda').$$

In particular, $J^V_{\leq}(\lambda) = J^V(\lambda)$ for all $\lambda \geq 0$.

Remark 4: The facts $J^U_\leq(\lambda) = J^U(\lambda)$ and that $J^U_\leq(\lambda)$ always has a minimizer do <u>not</u> imply that $J^U(\lambda)$ also has minimizers! This is due to the reason that minimizers for $J^U_\leq(\lambda)$ may have mass $< \lambda$.

Proof: We start with a proof of (b). Since $\mathcal{E}^0(\phi) \geq 0$ for all $\phi \in S(\lambda)$ we have $J^0(\lambda) \geq 0$. We will prove $J^0(\lambda) = 0$ by constructing a sequence $\phi_n \in S(\lambda)$ with $\mathcal{E}^0(\phi_n) \to 0$ for $n \to \infty$.

Fix a function $\phi \in S(\lambda)$ and define $\phi_\eta(x) = \eta^{3/2} \phi(\eta x)$. We apply a change of variables to see that

$$\int |\eta^{3/2} \phi(\eta x)|^2 dx = \int |\phi(x)|^2 dx, \qquad (47)$$

that is, $\phi_\lambda \in S(\lambda)$. The same change of variables shows

$$\mathcal{E}^0(\phi_\eta) = \frac{\eta^2}{2}\int_{\mathbb{R}^3} |\nabla\phi(x)|^2\,dx + \eta^2\,\frac{3}{5}C_{TF}\int_{\mathbb{R}^3} |\phi(x)|^{10/3}\,dx$$

$$+\frac{\eta}{2}\int_{\mathbb{R}^6}\frac{|\phi(x)|^2\,|\phi(y)|^2}{|x-y|}\,d(x,y). \tag{48}$$

This implies

$$0 \le J^0(\lambda) \le \mathcal{E}^0(\phi_\eta) \xrightarrow{\eta\to 0} 0, \tag{49}$$

which proves $J^0(\lambda)=0$.

Next we prove (c). Choose $\varepsilon>0$ and two functions $\phi_1\in S(\lambda')$, $\phi_2\in S(\lambda-\lambda')$ that satisfy

$$\mathcal{E}^V(\phi_1)\le J^V(\lambda')+\varepsilon \quad \text{and} \quad \mathcal{E}^0(\phi_2)\le\varepsilon. \tag{50}$$

Using the density of $C_c^\infty(\mathbb{R}^3)$ in $H^1(\mathbb{R}^3)$ and the continuity of $\mathcal{E}^V$ w.r.t. the norm topology of $H^1(\mathbb{R}^3)$, we check that we may assume that $\phi_1,\phi_2\in C_c^\infty(\mathbb{R}^3)$.

Let us also define the function

$$\Psi_R(x) = \phi_1(x) + \phi_2(x+Rv) \tag{51}$$

for $R>0$ and some fixed vector $v \in \mathbb{R}^3$. For R large enough we have

$$\int_{\mathbb{R}^3} |\Psi_R(x)|^2 dx = \underbrace{\int_{\mathbb{R}^3} |\phi_1(x)|^2 dx}_{=\lambda'} + \underbrace{\int_{\mathbb{R}^3} |\phi_2(x)|^2 dx}_{\lambda-\lambda'} = \lambda, \tag{52}$$

that is, $\Psi_R \in S(\lambda)$. A short calculation shows

$$J^U(\lambda) \leq \mathcal{E}^U(\Psi_R) = \mathcal{E}^U(\phi_1) + \mathcal{E}^0(\phi_2) + \int_{\mathbb{R}^3} U(x-Rv)\, |\phi_2(x)|^2 dx$$

$$+ \int_{\mathbb{R}^6} \frac{|\phi_1(x)|^2\, |\phi_2(y)|^2}{|x-y+Rv|} d(x,y)$$

$$\leq J^U(\lambda') + 2\varepsilon + \int_{\mathbb{R}^3} U(x-Rv)\, |\phi_2(x)|^2 dx \tag{53}$$

$$+ \int_{\mathbb{R}^6} \frac{|\phi_1(x)|^2\, |\phi_2(y)|^2}{|x-y+Rv|} d(x,y).$$

We use that Φ_1 and Φ_2 have compact support to show that the last two terms on the r.h.s. converge to 0 for $R \to \infty$. Hence,

$$J^U(\lambda) \leq J^U(\lambda') + 2\varepsilon. \qquad (54)$$

When we take the limit $\varepsilon \to 0$ on both sides, this proves the claim. It remains to prove part (a).

To prove the continuity of $\lambda \mapsto J^U(\lambda)$, we choose a sequence $\lambda_n \geq 0$ with $\lambda_n \to \lambda \geq 0$ and we first assume that $\lambda > 0$. We also choose two sequences $\{\Phi_n\}_{n=1}^{\infty}$ and $\{\Psi_n\}_{n=1}^{\infty}$ with $\Phi_n \in S(\lambda_n)$ and $\Psi_n \in S(\lambda)$ s.t.

$$\left| \mathcal{E}^U(\Phi_n) - J^U(\lambda_n) \right| \leq \frac{1}{n} \quad \text{and} \quad \left| \mathcal{E}^U(\Psi_n) - J^U(\lambda) \right| \leq \frac{1}{n}. \qquad (55)$$

We know from point (c) that $J^U(\lambda_n) \leq J^U\left(\inf_{n \geq 1} \lambda_n\right)$, and hence $J^U(\lambda_n)$ is a bounded sequence. By (55) the same is true for $\mathcal{E}^U(\Phi_n)$ and $\mathcal{E}^U(\Psi_n)$ and we conclude with the coercivity of $\mathcal{E}^U$ that $\{\phi_n\}_{n=1}^{\infty}$ and $\{\psi_n\}_{n=1}^{\infty}$ are bounded in $H^1(\mathbb{R}^3)$. This implies

$$\lim_{n\to\infty} \left| \mathcal{E}^U\left(\sqrt{\frac{\lambda_n}{\lambda}}\,\psi_n\right) - \mathcal{E}^U(\psi_n) \right| = 0$$

$$= \lim_{n\to\infty} \left| \mathcal{E}^U\left(\sqrt{\frac{\lambda}{\lambda_n}}\,\phi_n\right) - \mathcal{E}^U(\phi_n) \right| . \qquad (56)$$

We also have

$$J^U(\lambda_n) \le \mathcal{E}^U\left(\sqrt{\frac{\lambda_n}{\lambda}}\,\psi_n\right) \le J^U(\lambda) + \frac{1}{n} + \left| \mathcal{E}^U\left(\sqrt{\frac{\lambda_n}{\lambda}}\,\psi_n\right) - \mathcal{E}^U(\psi_n) \right| \quad (57)$$

as well as

$$J^U(\lambda) - \left| \mathcal{E}^U\left(\sqrt{\frac{\lambda}{\lambda_n}}\,\phi_n\right) - \mathcal{E}^U(\phi_n) \right| \le \mathcal{E}^U(\phi_n) \le J^U(\lambda_n) + \frac{1}{n}. \quad (58)$$

If we take the $\limsup_{n\to\infty}$ on both sides of (57) and the $\liminf_{n\to\infty}$ on both sides of (58), and use (56), we find

$$\limsup_{n\to\infty} J^U(\lambda_n) \le J^U(\lambda) \quad \text{and} \quad J^U(\lambda) \le \liminf_{n\to\infty} J^U(\lambda_n). \quad (59)$$

We conclude that $\lim_{n\to\infty} J^U(\lambda_n) = J^U(\lambda)$ if $\lambda > 0$.

It remains to consider the case $\lambda = 0$. In this case we have

$$\int_{\mathbb{R}^3} |\Phi_n(x)|^2 dx = \lambda_n \xrightarrow{n\to\infty} 0. \tag{60}$$

Since $\{\Phi_n\}_{n=1}^{\infty}$ is bounded in $H^1(\mathbb{R}^3)$ it has a weakly convergent subsequence $\{\Phi_{n_k}\}_{k=1}^{\infty}$. Using the weak continuity of the potential energy we conclude that

$$\int_{\mathbb{R}^3} U(x)\, |\Phi_{n_k}(x)|^2 dx \xrightarrow{k\to\infty} 0. \tag{61}$$

We have

$$\int_{\mathbb{R}^3} U(x)\, |\Phi_{n_k}(x)|^2 dx - \frac{1}{n} \leq \mathcal{E}^U(\Phi_n) - \frac{1}{n} \leq J^U(\lambda_n), \tag{62}$$

which implies $0 \leq \liminf_{n\to\infty} J^U(\lambda_n)$. On the other hand,

$\int_{\mathbb{R}^3} V(x)\,|\phi_n(x)|^2\,dx \leq 0$ implies

$$J^V(\lambda_n) \leq \mathcal{E}^V(\phi_n) \leq \mathcal{E}^0(\phi_n) \Rightarrow J^V(\lambda_n) \leq J^0(\lambda_n) = 0$$

$$\Rightarrow \limsup_{n\to\infty} J^V(\lambda_n) \leq 0. \qquad (63)$$

We conclude that $\lim_{n\to\infty} J^V(\lambda_n) = 0$, which proves Lemma 5.

$\blacksquare$

Step 3: Precompactness of minimizing sequences and binding inequalities

In the previous step we have proved that $\lambda \mapsto J^V(\lambda)$ is non-decreasing. In this step we show that if $J^V(\lambda) < J^V(\lambda')$ for all $\lambda' < \lambda$, then all minimizing sequences of $\mathcal{E}^V$ are precompact. In particular, a minimizer for $J^V(\lambda)$ must exist.

Proposition 1 (Binding inequalities and compactness of minimizing sequences): Let $\lambda \geq 0$. The following two statements are equivalent:

(a) All the minimizing sequences $\{\Phi_n\}_{n=1}^{\infty}$ for $J^V(\lambda)$ are precompact in $H^1(\mathbb{R}^3)$, that is, there exists a subsequence, which converges strongly in $H^1(\mathbb{R}^3)$.

(b) We have the binding inequalities

$$J^V(\lambda) < J^V(\lambda') \tag{64}$$

for all $0 \leq \lambda' < \lambda$.

Remark 5. In case of the Schrödinger equation we have seen that the condition $\inf_{\|\Psi\|=1} \mathcal{E}(\Psi) < 0$ implies compactness of minimizing sequences in H^1. Eq. (64) is the natural replacement for this condition in our setting.

Before we give the proof of Proposition 1, we state and prove the following lemma.

Lemma 6 (A criterion for compactness): Let $\{\phi_n\}_{n=1}^{\infty}$ be a minimizing sequence for $J^V(\lambda)$ with $\phi_n \to \phi$ weakly in $H^1(\mathbb{R}^3)$. Then $\phi_n \to \phi$ strongly in $H^1(\mathbb{R}^3)$ if and only if $\int_{\mathbb{R}^3} |\phi(x)|^2 \, dx = \lambda$.

Remark 6: Lemma 6 tells us that a minimizing sequence converges strongly in $H^1(\mathbb{R}^3)$ if no mass is lost at infinity.

Proof: If $\phi_n \to \phi$ strongly in $H^1(\mathbb{R}^3)$ then $\int |\phi(x)|^2 dx = \lambda$.

The difficult point is to prove the converse.

Let $\{\phi_n\}_{n=1}^{\infty}$ be a minimizing sequence for $J^V(\lambda)$ s.t. $\phi_n \rightharpoonup \phi$ weakly in $H^1(\mathbb{R}^3)$ and assume that $\int_{\mathbb{R}^3} |\phi(x)|^2 dx = \lambda$. Using the wlsc. of $\mathcal{E}^V$ we conclude that

$$J^V(\lambda) = \lim_{n\to\infty} \mathcal{E}^V(\phi_n) \geq \mathcal{E}^V(\underset{\in S(\lambda)}{\underset{\downarrow}{\phi}}) \geq J^V(\lambda). \qquad (65)$$

That is, ϕ is a minimizer for $J^V(\lambda)$ and $\lim_{n\to\infty} \mathcal{E}^V(\phi_n) = \mathcal{E}(\phi)$.

We have $\phi_n \rightharpoonup \phi$ in $L^2(\mathbb{R}^3)$ and $\|\phi_n\|_2^2 = \lambda = \|\phi\|_2^2$.

Hence

$$\|\phi_n - \phi\|_2^2 = \underset{\substack{\uparrow \\ L^2\text{- inner product} \\ \downarrow \\ (\phi,\psi) = \int_{\mathbb{R}^3} \overline{\phi}(x)\psi(x)\,dx}}{\langle \phi_n - \phi, \phi_n - \phi \rangle} = \langle \phi_n, \phi_n \rangle + \langle \phi, \phi \rangle + \underbrace{2\mathrm{Re}\langle \phi_n, \phi \rangle}_{\substack{n\to\infty \\ \to 2\mathrm{Re}(\phi,\phi) \text{ by} \\ \text{weak convergence.}}} \qquad (66)$$

We conclude that $\|\phi_n - \phi\|_2 \xrightarrow{n\to\infty} 0$.

By interpolation we have

$$\|\phi_n - \phi\|_p \leq \|\phi_n - \phi\|_2^{\theta} \, \|\phi_n - \phi\|_6^{1-\theta} \qquad (67)$$

for $\frac{1}{p} = \frac{\theta}{2} + \frac{1-\theta}{6}$. Moreover, the Sobolev inequality shows that $\|\phi_n - \phi\|_6 \leq \text{const.}\left(\|\nabla\phi_n\|_2 + \|\nabla\phi\|_2\right)$. The r.h.s. is uniformly bounded because $\{\phi_n\}_{n=1}^{\infty}$ is a bounded sequence in $H^1(\mathbb{R}^3)$ (follows from the coercivity of $\mathcal{E}^V$). We conclude that

$$\|\phi_n - \phi\|_p \xrightarrow{n\to\infty} 0 \quad \text{for} \quad 2 \leq p < 6. \qquad (68)$$

In particular,

$$\lim_{n\to\infty} \int_{\mathbb{R}^3} |\phi_n(x)|^{10/3} dx = \int_{\mathbb{R}^3} |\phi(x)|^{10/3} dx. \qquad (69)$$

We also have

$$\left| \int_{\mathbb{R}^6} \frac{|\Phi_n(x)|^2 \, |\Phi_n(y)|^2}{|x-y|} \, d(x,y) - \int_{\mathbb{R}^6} \frac{|\Phi(x)|^2 \, |\Phi(y)|^2}{|x-y|} \, d(x,y) \right|$$

$$= \left| \int_{\mathbb{R}^6} \frac{\left(|\Phi_n(x)|^2 - |\Phi(x)|^2 \right)\left(|\Phi_n(y)|^2 + |\Phi(y)|^2 \right)}{|x-y|} \, d(x,y) \right|$$

$$\leq \int_{\mathbb{R}^6} \frac{\left| \, |\Phi_n(x)|^2 - |\Phi(x)|^2 \right| \left(|\Phi_n(y)|^2 + |\Phi(y)|^2 \right)}{|x-y|} \, d(x,y)$$

$$\leq \left(\int_{\mathbb{R}^3} \underbrace{\left| \, |\Phi_n(x)|^2 - |\Phi(x)|^2 \right|}_{\left(|\Phi_n(x)| - |\Phi(x)|\right)\left(|\Phi_n(x)| + |\Phi(x)|\right)} dx \right) \underbrace{\left(\int_{\mathbb{R}^3} \left[|\nabla\Phi_n(x)|^2 + |\nabla\Phi(x)|^2 + \tfrac{1}{4}|\Phi_n(x)|^2 + \tfrac{1}{4}|\Phi(x)|^2 \right] dx \right)}_{\text{uniformly bounded in } n \in \mathbb{N}}$$

Kato's inequality,
See p. 17

$$\leq \text{const.} \left\| \underbrace{|\Phi_n| - |\Phi|}_{\leq |\Phi_n - \Phi|} \right\|_2 \Big(\underbrace{\|\Phi_n\|_2 + \|\Phi\|_2}_{2\lambda} \Big) \leq 2\lambda \, \text{const.} \, \|\Phi_n - \Phi\|_2 \xrightarrow{n \to \infty} 0. \qquad (70)$$

We have thus shown that all terms in $\mathcal{E}^V(\phi_n)$ converge to their counterparts with ϕ_n replaced by ϕ for $n\to\infty$, except for $\int_{\mathbb{R}^3} |\nabla\phi_n(x)|^2 dx$. However, since $\mathcal{E}^V(\phi_n) \to \mathcal{E}^V(\phi)$ for $n\to\infty$, also this term must obey

$$\lim_{n\to\infty} \int_{\mathbb{R}^3} |\nabla\phi_n(x)|^2 dx = \int_{\mathbb{R}^3} |\phi(x)|^2 dx. \tag{71}$$

With the same argument as in (66) we conclude that

$$\lim_{n\to\infty} \| \nabla\phi_n - \nabla\phi \|_2 = 0. \tag{72}$$

This proves the strong convergence of ϕ_n to ϕ in $H^1(\mathbb{R}^3)$.

$\blacksquare$

Having the above lemma at hand, we are prepared for the proof of Proposition 1.

<u>Proof of Proposition 1:</u> We start with the implication $[(a) \Rightarrow (b)] \Leftrightarrow [\neg(b) \Rightarrow \neg(a)]$. We recall that $J^V(\lambda') \le J^V(\lambda)$ for $\lambda' > \lambda$, that is, we need to assume $J^V(\lambda') = J^V(\lambda)$ for $\lambda' > \lambda$. The goal is to find a minimizing sequence $\{\Psi_n\}_{n=1}^{\infty}$ with $\Psi_n \in S(\lambda)$ for $J^V(\lambda)$ that is not precompact. We will choose Ψ_n s.t. $\Psi_n \rightharpoonup \varphi$ in $H^1(\mathbb{R}^3)$ with $\int_{\mathbb{R}^3} |\varphi(x)|^2 dx \le \lambda' < \lambda$. Clearly such a minimizing sequence cannot be precompact.

We choose $\Psi_n(x) = \Phi_1^n(x) + \Phi_2^n(x + R_n v)$ as in the proof of Lemma 5, where $\{\Phi_1^n\}_{n=1}^{\infty}$ with $\Phi_1^n \in S(\lambda')$ is a minimizing sequence for $J^V(\lambda')$ and $\Phi_2^n \in S(\lambda - \lambda')$ is a minimizing sequence for $J^0(\lambda - \lambda') = 0$. We can assume that all functions have compact support and that $R_n \to \infty$ fast enough s.t. the distance between the supports of Φ_1^n and $\Phi_2^n(\cdot - R_n v)$ goes to infinity and $\Phi_2^n(\cdot + R_n) \rightharpoonup 0$ in $H^1(\mathbb{R}^3)$. By passing to a subsequence we may also assume that $\phi_1^n \rightharpoonup \phi$ weakly in $H^1(\mathbb{R}^3)$, which implies $\Psi_n \rightharpoonup \phi$. Since $\phi_1^n \in S(\lambda')$ we have $\phi \in S_{\leq}(\lambda')$. This proves the above implication.

Next we assume $J^V(\lambda) < J^V(\lambda')$ holds for $0 \leq \lambda' < \lambda$ and we need to show that all minimizing sequences are precompact. To that end, let $\{\Phi_n\}_{n=1}^{\infty}$ be a minimizing sequence for $J^V(\lambda)$. With the coercivity of $\mathcal{E}^V$ we conclude that $\{\Phi_n\}_{n=1}^{\infty}$ is bounded in $H^1(\mathbb{R}^3)$, that is, it has a weakly convergent subsequence $\Phi_{n_k} \rightharpoonup \phi$. We denote $\lambda' = \int_{\mathbb{R}^3} |\phi(x)|^2 dx$. Using the wlsc. of $\mathcal{E}^V$, we see that

$$J^V(\lambda) = \lim_{n\to\infty} \mathcal{E}^V(\Phi_n) \geq \mathcal{E}^V(\phi). \tag{73}$$

Since $\phi \in S(\lambda')$ we also have $\mathcal{E}^V(\phi) \geq J^V(\lambda')$. In combination, these two bounds show

$$J^V(\lambda') \leq J^V(\lambda). \tag{74}$$

By assumption $J^V(\lambda) < J^V(\lambda')$ if $0 \leq \lambda' < \lambda$. We conclude that $\int_{\mathbb{R}^3} |\phi(x)|^2 = \lambda' = \lambda$. An application of Lemma 6 shows that $\{\phi_n\}_{n=1}^{\infty}$ converges strongly in $H^1(\mathbb{R}^3)$. This proves Proposition 1. $\blacksquare$

Step 4: The Euler-Lagrange equation

In this section we discuss some elementary properties of minimizers. They are captured in the following proposition.

Proposition 2 (Euler–Lagrange equation): Let ϕ be a minimizer of $J^V(\lambda)$ for some $\lambda > 0$. Then $\phi \in H^2(\mathbb{R}^3)$, $\phi = z|\phi|$ for some $z \in \mathbb{C}$ with $|z| = 1$ and there is a $z \in \mathbb{C}$, $|z| = 1$ s.t. $z\,\phi(x) > 0$ for all $x \in \mathbb{R}^3$.

Furthermore, ϕ solves the nonlinear equation

$$\left(-\frac{\Delta}{2} + V + C_{TF}\,|\phi|^{4/3} + |\phi|^2 * \frac{1}{|x|}\right)\phi = \mu\phi \tag{75}$$

for some $\mu \in \mathbb{R}$ with $\mu \leq 0$. More precisely, μ is the lowest eigenvalue of the self-adjoint operator

$$H_\phi = -\frac{\Delta}{2} + V + C_{TF}\,|\phi|^{4/3} + |\phi|^2 * \frac{1}{|x|}. \tag{76}$$

Remark 7: Proposition 2 implies that H_ϕ has always one nonpositive eigenvalue. We later show that $\mu < 0$ except at one point. This is the largest point λ, where $J^V(\lambda)$ has a minimizer.

Remark 8: One can prove that functions in $H^2(\mathbb{R}^3)$ are actually continuous. Accordingly, the statement $|\phi(x)|>0$ for all $x\in\mathbb{R}^3$ makes sense.

Proof of Proposition 2: The proof is very similar to that we gave for the Schrödinger equation.
Let $\phi\in S(\lambda)$ be a minimizer of $J^V(\lambda)$. For $\chi\in H^1(\mathbb{R}^3)$ and $\varepsilon>0$ we choose

$$\phi_\varepsilon(x)=\sqrt{\lambda}\,\frac{\phi(x)+\varepsilon\chi(x)}{\underbrace{\|\phi+\varepsilon\chi\|_2}_{=\left(\lambda+2\varepsilon\,\mathrm{Re}\,\langle\phi,\chi\rangle+\varepsilon^2\|\chi\|^2\right)^{1/2}}}\overset{\text{Taylor exp.}}{=}\phi+\varepsilon\left(\chi-\frac{\mathrm{Re}\,\langle\phi,\chi\rangle}{\lambda}\phi\right)+R_\varepsilon, \tag{77}$$

with $\|R_\varepsilon\|_{H^1}\le C\varepsilon^2$. We note that $\phi_\varepsilon\in S(\lambda)$, and hence

$$\mathcal{E}^V(\phi_\varepsilon)\ge J^V(\lambda)=\mathcal{E}^V(\phi). \tag{78}$$

We expand $\mathcal{E}^V(\phi_\varepsilon)$ in powers of ε and find

$$\mathcal{E}^V(\phi_\varepsilon) = \mathcal{E}^V(\phi) + 2\varepsilon \operatorname{Re}\Big(\frac{1}{2}\int_{\mathbb{R}^3} \overline{\nabla\phi(x)}\cdot\nabla\chi(x)\,dx$$

$$+ \int_{\mathbb{R}^3} \Big(V(x) + C_{TF}\,|\phi(x)|^{4/3} + |\phi|^2 * \frac{1}{|\cdot|}(x)\Big)\,\overline{\phi(x)}\,\chi(x)\,dx$$

$$-\mu\langle\phi,\chi\rangle\Big) + O(\varepsilon^2), \tag{79}$$

where

$$\mu = \frac{1}{\lambda}\int_{\mathbb{R}^3}\Big(\frac{1}{2}|\nabla\phi(x)|^2 + V(x)|\phi(x)|^2 + C_{TF}\,|\phi(x)|^{\frac{10}{3}}\Big)\,dx$$

$$+ \frac{1}{\lambda}\int_{\mathbb{R}^6}\frac{|\phi(x)|^2\,|\phi(y)|^2}{|x-y|}\,d(x,y). \tag{80}$$

The term proportional to ε in (79) must vanish because the map $\varepsilon \mapsto \mathcal{E}^V(\phi_\varepsilon)$ admits a minimum at $\varepsilon = 0$. When we replace χ by $i\chi$ in the above analysis, we obtain (79) with the real part replaced by the imaginary part. We thus obtain

$$\frac{1}{2}\int_{\mathbb{R}^3} \overline{\nabla\phi(x)}\,\nabla\chi(x)\,dx + \int_{\mathbb{R}^6}\Big(V(x) + C_{TF}\,|\phi(x)|^{4/3} + |\phi|^2 * \frac{1}{|\cdot|}(x)\Big)\,\overline{\phi(x)}\,\chi(x)\,dx$$

$$= \mu \int_{\mathbb{R}^3} \overline{\phi(x)}\,\chi(x)\,dx \qquad (81)$$

for all $\chi \in H^1(\mathbb{R}^3)$. This proves that ϕ satisfies the

$$\Big(-\frac{\Delta}{2} + V(x) + C_{TF}\,|\phi(x)|^{4/3} + |\phi|^2 * \frac{1}{|\cdot|}(x)\Big)\phi(x) = \mu\,\phi(x) \qquad (82)$$

in the sense of distributions (actually also when tested against a function in $H^1(\mathbb{R}^3)$). We use $\phi \in H^1(\mathbb{R}^3) \subset L^2(\mathbb{R}^3) \cap L^6(\mathbb{R}^3)$ to check that $|\phi|^{4/3} \in L^2(\mathbb{R}^3)$ and $|\phi|^2 * \frac{1}{|\cdot|} \in L^\infty(\mathbb{R}^3)$, which implies $|\phi|^2 * \frac{1}{|\cdot|}\,\phi \in L^2(\mathbb{R}^3)$. To see that $V\phi \in L^2(\mathbb{R}^3)$ we estimate

$$\int_{\mathbb{R}^3} |V(x)\phi(x)|^2\,dx = \sum_{m_1,m_2=1}^{M} Z_{m_1} Z_{m_2} \int_{\mathbb{R}^3} \frac{1}{|x-R_{m_1}|}\,\frac{1}{|x-R_{m_2}|}\,|\phi(x)|^2\,dx$$

$$\leq \sum_{m_1,m_2=1}^{M} Z_{m_1} Z_{m_2} \frac{1}{2} \left[\int_{\mathbb{R}^3} \frac{1}{|x-R_{m_1}|^2} |\phi(x)|^2 \, dx + \int_{\mathbb{R}^3} \frac{1}{|x-R_{m_2}|^2} |\phi(x)|^2 \, dx \right]$$

$$\leq \sum_{m_1,m_2=1}^{M} Z_{m_1} Z_{m_2} \frac{1}{8} \left[\int_{\mathbb{R}^3} |\nabla\phi(x+R_{m_1})|^2 \, dx + \int_{\mathbb{R}^3} |\nabla\phi(x+R_{m_2})|^2 \, dx \right]$$

Hardy's inequality on p. 83

$$\leq \frac{Z^2}{4} \int_{\mathbb{R}^3} |\nabla\phi(x)|^2 \, dx.$$

Accordingly, the distributional Laplacian of ϕ is given by a function in $L^2(\mathbb{R}^3)$ (use Eq. (82)) and we conclude that $\phi \in H^2(\mathbb{R}^3)$ (Please check the details of this claim!).

Next, we show $\mu \leq 0$. Let $\phi \in S(\lambda)$ be a minimizer of $\mathcal{E}^V$ and choose $\varepsilon > 0$ s.t. $1-\varepsilon > 0$. We have

$$\mathcal{E}^V\big((1-\varepsilon)\phi\big) = \mathcal{E}^V(\phi) - 2\varepsilon \operatorname{Re}\langle H_\phi \phi, \phi\rangle + O(\varepsilon^2)$$

$$= J^V(\lambda) - 2\varepsilon\mu\lambda + O(\varepsilon^2) \tag{83}$$

with H_ϕ in (76). Since $(1-\varepsilon)\phi \in S\big((1-\varepsilon)^2\lambda\big)$ we also have

$$\mathcal{E}^V\big((1-\varepsilon)\phi\big) \geq J^V\big((1-\varepsilon)^2\lambda\big) \geq J^V(\lambda) \tag{84}$$

by Lemma 5. Putting (83) and (84) together, we find

$$J^V(\lambda) - 2\varepsilon\mu\lambda + O(\varepsilon^2) \geq J^V(\lambda)$$

$$\Leftrightarrow \quad - 2\varepsilon\mu\lambda + O(\varepsilon^2) \geq 0$$

$$\Rightarrow \quad \mu \leq 0. \tag{85}$$

It remains to show that μ is the lowest eigenvalue of H_ϕ, that $\phi = z|\phi|$ with $|z|=1$ and $|\phi| > 0$.

For all these statements we need to know that if ϕ is a minimizer, then $|\phi|$ is a minimizer. As in the case of the Schrödinger equation this follows from the convexity inequality for gradients, which implies

$$\mathcal{E}^U(\phi) \geq \mathcal{E}^U(|\phi|). \tag{86}$$

As ϕ, $|\phi|$ solves the equation

$$\left(-\frac{\Delta}{2} + U(x) + C_{TF}\,|\phi(x)|^{4/3} + |\phi|^2 * \frac{1}{|\cdot|}(x)\right)|\phi(x)| = \mu'|\phi(x)|, \tag{87}$$

Using $\int |\nabla\phi(x)|^2 dx = \int |\nabla|\phi(x)||^2 dx$ and (80) we conclude that $\mu' = \mu$, that is,

$$\left(-\frac{\Delta}{2} + W_\phi\right)|\phi| = \mu\,|\phi| \tag{88}$$

with $W_\phi(x) = U(x) + C_{TF}|\phi(x)|^{4/3} + |\phi|^2 * \frac{1}{|\cdot|}(x)$. From the Sobolev embedding $H^2(\mathbb{R}^3) \subset L^\infty(\mathbb{R}^3)$ we know that $|\phi|^{4/3} \in L^\infty(\mathbb{R}^3)$ and that $|\phi|^2 * \frac{1}{|\cdot|} \in L^\infty(\mathbb{R}^3)$.

From Theorem 5.5.2. we know that (We assumed $V \in L^2(\mathbb{R}^3)$, but $V \in L^1_{loc}(\mathbb{R}^3)$ is actually sufficient. We will use this version without proof.)

Let $V \in L^1_{loc}(\mathbb{R}^3)$ and assume additionally that there exists a constant $C > 0$ s.t. $V(x) \leq C \quad \forall\, x \in \mathbb{R}^3$ holds. Then the lowest eigenvalue of $-\Delta + V(x)$, if it exists, has multiplicity one and its associated eigenfunction is strictly positive (up to a phase factor).

Remark 9: We proved the existence of a minimizer for e_0 only if $e_0 < 0$. But if $e_0 = 0$ and we know that a minimizer exists, then our proof shows that it is unique and strictly positive (up to a phase).

Clearly we can apply the above statement to $-\Delta + W_\phi$. Let us denote by μ_1 the lowest eigenvalue of $-\Delta + W_\phi$ and by ϕ_1 the corresponding eigenfunction.

We may assume that $\phi_1 > 0$. If $\mu \neq \mu_1$ then ϕ_1 and $|\phi|$ need to be orthogonal in $L^2(\mathbb{R}^3)$ because

$$\langle |\phi|, H_\phi \phi_1 \rangle = \langle |\phi|, \phi_1 \rangle \mu_1$$

$$\| \leftarrow \text{integration by parts}$$

$$\langle H_\phi |\phi|, \phi_1 \rangle = \mu \langle |\phi|, \phi_1 \rangle . \tag{89}$$

But this is impossible because

$$\int_{\mathbb{R}^3} \underbrace{|\phi(x)|}_{\geq 0} \underbrace{\phi_1(x)}_{>0} \, dx > 0 . \tag{90}$$

We conclude that $\mu = \mu_1$. Since μ_1 has multiplicity one, $|\phi|$ is the unique positive associated eigenfunction. In particular, $|\phi| > 0$ and $\phi = z|\phi|$ with $z \in \mathbb{C}$, $|z| = 1$.

This ends the proof of Proposition 2.

Step 5: Convexity and consequences

We have seen in Step 3 that all minimizing sequences are precompact if certain binding inequalities hold. In this section we will use convexity properties of $\mathcal{E}^U$ to prove the existence of λ_c (see fig 1). Before we come to this point, we prove the following lemma.

Lemma 7 (Convexity property of $\mathcal{E}^U$): Let $\phi_1, \phi_2 \in H^1(\mathbb{R}^3)$ and $t \in [0,1]$. We have

$$\mathcal{E}^U\left(\sqrt{t|\phi_1|^2 + (1-t)|\phi_2|^2}\right) \leq t\,\mathcal{E}^U(\phi_1) + (1-t)\,\mathcal{E}^U(\phi_2). \quad (S1)$$

If $t \in (0,1)$ there is equality if and only if $|\phi_1| = |\phi_2|$.

Proof: To prove the above claim we show that $\mathcal{E}^U$ is convex as a function of $\rho(x) = |\phi(x)|^2$. We start by noting that the map

$$\rho \mapsto \int_{\mathbb{R}^3} \rho^{5/3}(x)\, dx \tag{S2}$$

is strictly convex because the map $x \ni [0,\infty) \mapsto x^{5/3}$ is.

To see that the map $\rho \mapsto \int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|}\, d(x,y)$ is strictly convex we write it in Fourier space as

$$\int_{\mathbb{R}^6} \frac{\rho(x)\rho(y)}{|x-y|}\, d(x,y) = 4\pi \int_{\mathbb{R}^3} \frac{|\hat{\rho}(k)|^2}{|k|^2}\, dk. \tag{S3}$$

Eq. (S3) can be justified e.g. with Exercise 6 on sheet no. 2. From the convexity inequality for gradients we know that

$$\int_{\mathbb{R}^3} \left|\nabla\sqrt{t\rho_1(x) + (1-t)\rho_2(x)}\right|^2 dx \tag{S4}$$

$$\leq t \int_{\mathbb{R}^3} \left|\nabla\sqrt{\rho_1(x)}\right|^2 dx + (1-t)\int_{\mathbb{R}^3} \left|\nabla\sqrt{\rho_2(x)}\right|^2 dx$$

holds. In conclusion, these considerations prove (S1). The case of equality is a consequence of the strict convexity of the maps in (S2) and (S3). This proves the claim. ∎

Using the above lemma we can derive two immediate but important conclusions.

Corollary 2 (Convexity of $\lambda \mapsto J^U(\lambda)$): The function $\lambda \mapsto J^U(\lambda) = J^U_{\leq}(\lambda)$ is convex and nonincreasing.

Proof: The fact that $J^U(\lambda)$ is nonincreasing has already been proved in Lemma 5. Let $\lambda_1, \lambda_2 \geq 0$ and $t \in [0,1]$. We assume that $\phi_1 \in S(\lambda_1)$ and $\phi_2 \in S(\lambda_2)$ are s.t. $J^U(\lambda_j) \leq \mathcal{E}^U(\phi_j) + \varepsilon$ for $j = 1,2$. Eq. (48)

implies

$$\mathcal{J}^V\big(t\lambda_1+(1-t)\lambda_2\big) \leq \mathcal{E}^V\left(\sqrt{t\,|\phi_1(x)|^2+(1-t)\,|\phi_2(x)|^2}\right)$$

$$\leq t\,\mathcal{E}^V(\phi_1)+(1-t)\,\mathcal{E}(\phi_2)$$

$$\leq t\,\mathcal{J}^V(\lambda_1)+(1-t)\,\mathcal{J}^V(\lambda_2)+2\varepsilon. \tag{55}$$

The claimed convexity follows when we let $\varepsilon \to 0$.

Remark 10: In Lemma 5 we also proved the continuity of $\lambda \mapsto \mathcal{J}^V(\lambda)$. Note that the statement also follows from the convexity of this map. That is, we have seen two ways of proving continuity.

Corollary 3 (Uniqueness): When they exist, minimizers for $\mathcal{J}^V(\lambda)$ and $\mathcal{J}^V_{\leq}(\lambda)$ are unique up to a phase factor, that is, all minimizers are of the form

$z\phi$ with some fixed ϕ and $z \in \mathbb{C}$ with $|z| = 1$.

Proof: Let ϕ_1 and ϕ_2 be two minimizers for $J^V_{\leq}(\lambda)$.

ϕ_1 and ϕ_2 are also minimizers for $J^V(\lambda_1)$ and $J^V(\lambda_2)$ with $\lambda_j = \int_{\mathbb{R}^3} |\phi_j(x)|^2 dx \leq \lambda$. From Proposition 2 we know that $\phi_1 = z_1 |\phi_1|$ with $|\phi_1| > 0$ and $\phi_2 = z_2 |\phi_2|$ with $|\phi_2| > 0$. It therefore suffices to show that $|\phi_1| = |\phi_2|$.

An application of Lemma 7 implies

$$
\begin{aligned}
J^V_{\leq}(\lambda) &\leq \mathcal{E}^V\left(\sqrt{t|\phi_1|^2 + (1-t)|\phi_2|^2}\right) \\
&\leq t \underbrace{\mathcal{E}^V(|\phi_1|)}_{= J^V_{\leq}(\lambda)} + (1-t) \underbrace{\mathcal{E}^V(|\phi_2|)}_{= J^V_{\leq}(\lambda)} = J^V_{\leq}(\lambda) \qquad (86)
\end{aligned}
$$

for all $t \in (0,1)$. Equality must hold in (86) and it follows that $|\phi_1| = |\phi_2|$. The proof for $J^V(\lambda)$ is the same. $\blacksquare$

Since we know that $\mathcal{J}^V_{\leq}(\lambda)$ has a minimizer for all $\lambda \geq 0$ (see Corollary 1), we have existence and uniqueness for $\mathcal{J}^V_{\leq}(\lambda)$. It remains to study $\mathcal{J}^V(\lambda)$.

Proposition 3 (Existence of a critical λ_c):

There exists a number $0 \leq \lambda_c \leq \infty$ s.t. the following holds:

For $0 \leq \lambda \leq \lambda_c$:

- the variational problems $\mathcal{J}^V(\lambda)$ and $\mathcal{J}^V_{\leq}(\lambda)$ admit the same unique minimizer $\Phi_\lambda > 0$ (up to a phase factor),
- all minimizing sequences for $\mathcal{J}^V(\lambda)$ and $\mathcal{J}^V_{\leq}(\lambda)$ are precompact in $H^1(\mathbb{R}^3)$.

For $\lambda > \lambda_c$:

- there is no minimizer for $\mathcal{J}^V(\lambda)$,
- if $\{\Phi_n\}_{n=1}^{\infty}$ is a minimizing sequence for $\mathcal{J}^V(\lambda)$

with $\phi_n \geq 0$ for all n, then we must have $\phi_n \rightharpoonup \phi_{\lambda_c}$ weakly in $H^1(\mathbb{R}^3)$,

• the variational problem $J^V_{\leq}(\lambda)$ admits ϕ_{λ_c} as unique minimizer (up to a phase).

Proof: The fact that the map $\lambda \mapsto J^V(\lambda)$ is convex and nonincreasing implies directly that there is a $0 \leq \lambda_c \leq \infty$ s.t. J^V is strictly decreasing on $[0, \lambda_c]$ and constant on $[\lambda_c, \infty)$. When $0 \leq \lambda \leq \lambda_c$, the binding inequality

$$J^V(\lambda) < J^V(\lambda') \quad \text{is satisfied for } 0 \leq \lambda' < \lambda \tag{97}$$

and we know from Proposition 1 that all minimizing sequences are precompact and there is a minimizer. Since (97) holds for J^V it is clear that the same inequalities hold for $J^V_{\leq}(\lambda) = J^V(\lambda)$. By Corollary 3 minimizers are unique up to a phase factor. By Proposition 2, the minimizer can be chosen positive. In the following we denote by ϕ_λ the unique positive minimizer for $J^U(\lambda)$ and $J^U_{\leq}(\lambda)$, for $0 \leq \lambda \leq \lambda_c$.

When $\lambda > \lambda_c$ we have $J^U(\lambda) = J^U(\lambda_c)$, and hence the minimizer ϕ_{λ_c} for λ_c is also a minimizer for $J^U_{\leq}(\lambda)$. By uniqueness it is the only one (up to a phase). The problem $J^U(\lambda)$ cannot have a minimizer for $\lambda > \lambda_c$, as this would provide another minimizer for $J^U_{\leq}(\lambda)$ and contradict uniqueness.

Finally, let us show that any minimizing sequence $\{\phi_n\}_{n=1}^{\infty}$ with $\phi_n \geq 0$ and $\lambda > \lambda_c$ is s.t. $\phi_n \to \phi_{\lambda_c}$ in $H^1(\mathbb{R}^3)$: Since $\{\phi_n\}_{n=1}^{\infty}$ is bounded in $H^1(\mathbb{R}^3)$ there exists a subsequence $\{\phi_{n_k}\}_{k=1}^{\infty}$ with $\phi_{n_k} \rightharpoonup \phi \in H^1(\mathbb{R}^3)$

weakly in $H^1(\mathbb{R}^3)$. By the w.l.s.c. of $\mathcal{E}^V$, we have

$$\liminf_{k\to\infty} \mathcal{E}^V(\phi_{n_k}) \geq \mathcal{E}^V(\phi) = J^V(\lambda') \tag{98}$$

$$\underset{}{\overset{\shortparallel}{J^V(\lambda)}} \underset{\lambda>\lambda_c}{\overset{\uparrow}{=}} J^V(\lambda_c). \qquad \lambda' = \int_{\mathbb{R}^3} |\phi(x)|^2 dx$$

We cannot have $\lambda' = \int_{\mathbb{R}^3} |\phi(x)|^2 dx < \lambda_c$ as this would imply $J^V(\lambda') \leq J^V(\lambda_c)$ and contradict the definition of λ_c (we have $J^V(\lambda) > J^V(\lambda_c)$ for $\lambda < \lambda_c$, see Proposition 1 and what we proved so far). Moreover, $\lambda' > \lambda_c$ would imply that $J^V(\lambda')$ has a minimizer, which contradicts our previous considerations. We conclude that $\lambda' = \lambda_c$. Eq. (98) therefore implies that ϕ is a minimizer for $J^V(\lambda_c)$. Since this minimizer is unique, we have $\phi = z\phi_{\lambda_c}$ for some $z \in \mathbb{C}$ with $|z| = 1$. By assumption, $\phi_n \geq 0$, which implies $\phi \geq 0$ as well as $z = 1$. This proves the claim. $\blacksquare$

We now come to the last step in the proof of Theorem 1.

Step 6: estimates on μ

To end the proof of Theorem 1 we need to show the following two lemmas.

Lemma 8: The Lagrange multiplier μ_λ in (75) satisfies $\mu_\lambda < 0$ if $0 < \lambda < \lambda_c$ and $\mu_{\lambda_c} = 0$.

Proof: We recall that $\mu_\lambda \leq 0$ for all $0 \leq \lambda \leq \lambda_c$.

Let us first show that $\mu_{\lambda_c} = 0$. We estimate for $\varepsilon > 0$

$$J^U(\lambda_c) = J^U\left((1+\varepsilon)^2\lambda_c\right) \leq \mathcal{E}^U\left((1+\varepsilon)\phi_{\lambda_c}\right)$$

Please carry out this computation in detail!

$$= J^U(\lambda_c) + 2\varepsilon\mu_{\lambda_c} + O(\varepsilon^2) \qquad (99)$$

$$\Leftrightarrow \quad 0 \leq 2\varepsilon\mu_{\lambda_c} + O(\varepsilon^2),$$

and hence $\mu_{\lambda_c} \geq 0$. In combination with $\mu_{\lambda_c} \leq 0$, this implies $\mu_{\lambda_c} = 0$.

Next we assume $0 < \lambda < \lambda_c$ and apply Lemma 7 (Convexity) with $0 \leq \varepsilon \leq 1$:

$$\mathcal{E}^U\left(\sqrt{(1-\varepsilon)\underset{\text{strictly positive}}{\phi_\lambda^2} + \varepsilon\,\phi_{\lambda_c}^2}\right) \leq (1-\varepsilon)J^U(\lambda) + \varepsilon\, J^U(\lambda_c). \qquad (100)$$

Using $\phi_\lambda > 0$ we expand

$$\sqrt{(1-\varepsilon)\phi_\lambda^2 + \varepsilon\,\phi_{\lambda_c}^2} = \phi_\lambda \sqrt{1 + \varepsilon\left(\frac{\phi_{\lambda_c}^2}{\phi_\lambda^2} - 1\right)}$$

$$\left[\begin{array}{l} f(x+h) = f(x) + f'(x)h + \frac{1}{2} f''(\xi) h^2 \quad \text{with} \quad \xi \in [x, x+h] \\ f(x) = \sqrt{x}, \quad f'(x) = \frac{1}{2} x^{-1/2}, \quad f''(x) = -\frac{1}{4} x^{-3/2} \\ \Rightarrow \sqrt{x+h} = \sqrt{x} + \frac{1}{2} \frac{h}{\sqrt{x}} - \frac{1}{8} \xi^{-3/2} h^2 \end{array}\right]$$

$$= \phi_\lambda + \frac{\varepsilon}{2} \left(\frac{\phi_{\lambda_c}^2}{\phi_\lambda} - \phi_\lambda \right) - \frac{1}{8} \xi^{-3/2} \varepsilon^2 \left(\phi_{\lambda_c}^2 - \phi_\lambda^2 \right)^2. \qquad (101)$$

$$\hookrightarrow \xi \in \left[1, 1 + \varepsilon \left(\phi_{\lambda_c}^2 - \phi_\lambda^2 \right) \right]$$

A careful analysis that uses (101) and that we motivate the reader to carry out explicitly in detail shows (see also the proof of Proposition 2, where similar techniques have been used)

$$\mathcal{E}^U\left(\sqrt{(1-\varepsilon)\phi_\lambda^2 + \varepsilon \phi_{\lambda_c}^2} \right) = J^U(\lambda) + \varepsilon \mu_\lambda \left\langle \phi_\lambda, \left(\frac{\phi_{\lambda_c}^2}{\phi_\lambda} - \phi_\lambda \right) \right\rangle + O(\varepsilon^2). \qquad (102)$$

In combination with (100) this implies

$$J^U(\lambda) + \varepsilon \mu_\lambda \left\langle \phi_\lambda , \left(\frac{\phi_{\lambda_c}^2}{\phi_\lambda} - \phi_\lambda \right) \right\rangle + O(\varepsilon^2)$$

$$\leq (1-\varepsilon) J^U(\lambda) + \varepsilon J^U(\lambda_c)$$

divide by ε and take $\varepsilon \to 0$

$$\Rightarrow \quad \mu_\lambda \underbrace{\left\langle \phi_\lambda , \left(\frac{\phi_{\lambda_c}^2}{\phi_\lambda} - \phi_\lambda \right) \right\rangle}_{\int_{\mathbb{R}^3} \phi_{\lambda_c}^2(x)\,dx - \int_{\mathbb{R}^3} \phi_\lambda^2(x)\,dx \;=\; \lambda_c - \lambda} \leq J^U(\lambda_c) - J^U(\lambda)$$

$$\Rightarrow \quad \mu_\lambda (\lambda_c - \lambda) \leq J^U(\lambda_c) - J^U(\lambda). \tag{103}$$

We have $\lambda < \lambda_c$ and $J^U(\lambda_c) - J^U(\lambda) < 0$, which implies $\mu_{\lambda_c} < 0$.

$\blacksquare$

In the next lemma we show that μ_λ is the derivative of $J^U(\lambda)$.

Lemma 8 (Derivative of $J^U(\lambda)$): The functions

$\lambda \mapsto \underset{\sim}{\phi_\lambda} \in H^1(\mathbb{R}^3)$ and $\lambda \mapsto \mu_\lambda$ are continuous on $[0, \lambda_c]$.
strictly positive

The function $\lambda \mapsto J^U(\lambda)$ is continuously differentiable on $[0, \lambda_c]$ and we have $(J^U)'(\lambda) = \mu_\lambda$.

Proof: Let $\{\lambda_n\}_{n=1}^\infty$ be a sequence with $\lambda_n \to \lambda \in [0, \lambda_c]$. From Lemma 5 (Continuity of $\lambda \mapsto J^U(\lambda)$) we know that $J^U(\lambda_n) \overset{n\to\infty}{\to} J^U(\lambda)$, and hence $\mathcal{E}^U(\phi_{\lambda_n}) \to J^U(\lambda)$. In other words, ϕ_{λ_n} is a minimizing sequence for $J^U(\lambda)$. From Proposition 1 we know that all minimizing sequences are precompact in $H^1(\mathbb{R}^3)$ if the relevant binding inequality is satisfied, which is the case for $\lambda \in [0, \lambda_c]$. We conclude that every subsequence of $\{\phi_{\lambda_n}\}_{n=1}^\infty$ has has subsequence that converges strongly in $H^1(\mathbb{R}^3)$

to some $\phi \in H^1(\mathbb{R}^3)$ (at this point the function ϕ may depend on the subsequence). Using the continuity of $\phi \mapsto \mathcal{E}^V(\phi)$ w.r.t. the strong topology of $H^1(\mathbb{R}^3)$ and $\phi_{\lambda_n} \geq 0$, we conclude that $\phi = \phi_\lambda$ (that is ϕ does <u>not</u> depend on the subsequence). Since every subsequence of $\{\phi_{\lambda_n}\}_{n=1}^{\infty}$ has a subsequence that converges to ϕ_λ we also conclude that $\phi_{\lambda_n} \to \phi_\lambda$ strongly in $H^1(\mathbb{R}^3)$. Here we used the fact statement $[\,\cdot\,]$ on p. 34.

When we combine this result and (103) we easily check that $\mu_{\lambda_n} \xrightarrow{n\to\infty} \mu_\lambda$.

It remains to show that $\lambda \mapsto J^U(\lambda)$ is differentiable and that $(J^U)'(\lambda) = \mu_\lambda$. We argue as in the proof of Lemma 8 to see that for all $\lambda, \lambda' \in [0, \lambda_c]$, we have

$$\mu_\lambda (\lambda' - \lambda) \leq J^U(\lambda') - J^U(\lambda). \tag{104}$$

Hence,

$$\mu_\lambda (\lambda_n - \lambda) \leq J^U(\lambda_n) - J^U(\lambda) \quad \text{and}$$
$$\mu_{\lambda_n} (\lambda - \lambda_n) \leq J^U(\lambda) - J^U(\lambda_n), \tag{105}$$

which implies (check this!)

$$\left| \mu_\lambda - \frac{J^U(\lambda_n) - J^U(\lambda)}{\lambda_n - \lambda} \right| \leq \left| \mu_{\lambda_n} - \mu_\lambda \right|. \tag{106}$$

With the continuity of the map $\lambda \mapsto \mu_\lambda$ we conclude that $(J^U)'(\lambda) = \mu_\lambda$. This proves Lemma 9 and also ends the proof of Theorem 1 on p. 26. $\blacksquare$

4. Estimates on λ_c

In Theorem 1 we have established the existence of $\lambda_c \in [0,\infty]$ s.t. $J^V(\lambda)$ has a minimizer for $0 \leq \lambda \leq \lambda_c$ and has no minimizer for $\lambda > \lambda_c$. In this section we show that $Z \leq \lambda_c \leq 2Z$ (Z denotes the nuclear charge, see the definition of $V(x)$).

The lower bound implies the stability of neutral and positively charged atoms and molecules in TFW theory, and the upper bound shows the instability of atoms with too many electrons.

Theorem 2 (Estimates on λ_c): Let

$$V(x) = -\sum_{m=1}^{M} \frac{z_m}{|x-R_m|} \tag{107}$$

with $z_m \in \mathbb{R}_+$ and $R_m \in \mathbb{R}^3$ and denote $Z = \sum_{i=1}^{m} z_m$.

Then the maximal number λ_c of electrons that the system can bind satisfies

$$Z \leq \lambda_c \leq 2Z. \tag{108}$$

Before we give a proof of the above theorem we state and prove one other theorem and one lemma that will be needed during its proof. We start with a statement called Newton's theorem.

Theorem 3 (Newton's theorem): Let ϱ be a radial function. Then (as soon as all the terms make sense)

$$\int_{\mathbb{R}^3} \frac{\varrho(y)}{|x-y|}\,dy = \int_{\mathbb{R}^3} \frac{\varrho(y)}{\max\{|x|,|y|\}}\,dy$$

$$= \int_{|x|\leq|y|} \frac{\varrho(y)}{|y|}\,dy + \frac{1}{|x|}\int_{|x|>|y|} \varrho(y)\,dy. \qquad (109)$$

Proof: For the sake of simplicity we will use the slight abuse of notation $\varrho(x) = \varrho(|x|)$. The function

$$\phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|}\varrho(y)\,dy \qquad (110)$$

is radial, and it therefore suffices to compute $\phi(re_3)$ with $r>0$. We pass to spherical coordinates and compute

$$\phi(re_3) = \int_{\mathbb{R}^3} \frac{\rho(y)}{|re_3 - y|}\, dy \qquad y = s \begin{pmatrix} \cos\theta \sin\varphi \\ \sin\theta \sin\varphi \\ \cos\varphi \end{pmatrix}$$

$$= \int_0^\infty s^2 \int_0^{2\pi} \int_0^{\pi} \sin\varphi \, \frac{\rho(s)}{\sqrt{s^2 - 2rs\cos\varphi + r^2}}\, d\varphi\, d\theta\, ds$$

$$|re_3 - y|^2 = |(s\cos\theta\sin\varphi, \sin\theta\sin\varphi, s\cos\varphi - r)|^2$$

$$= \underbrace{s^2\cos^2\theta\sin^2\varphi + s^2\sin^2\theta\sin^2\varphi}_{= s^2 \sin^2\varphi} + (s\cos\varphi - r)^2$$

$$= \underbrace{s^2\sin^2\varphi + s^2\cos^2\varphi}_{= s^2} - 2rs\cos\varphi + r^2$$

$$= 2\pi \int_0^\infty \int_{-1}^{1} \frac{\rho(s)}{\sqrt{s^2 - 2rst + r^2}}\, s^2\, ds\, dt$$

$$\left[\begin{array}{ll} t = \cos\varphi, & \varphi = 0 \Rightarrow t = 1 \\ dt = -\sin\varphi\, d\varphi, & \varphi = \pi \Rightarrow t = -1 \end{array}\right]$$

$$= 2\pi \int_0^\infty \int_{-1}^{1} \frac{1}{\sqrt{1+u^2-2ut}} \, \frac{\rho(s)}{\max\{r,s\}} \, dt \, s^2 ds. \qquad (111)$$

$$u = \frac{\min\{r,s\}}{\max\{r,s\}} \in [0,1] \, ;$$

$$\left(1+u^2-2ut\right) \max\{r,s\}^2 = \left[1 + \left(\frac{\min\{r,s\}}{\max\{r,s\}}\right)^2 - 2 \, \frac{\min\{r,s\}}{\max\{r,s\}} \, t \right] \times \max\{r,s\}^2$$

$$= \max\{r,s\}^2 + \min\{r,s\}^2 - 2 \min\{r,s\} \max\{r,s\} \, t$$

$$= \begin{cases} s^2 + r^2 - 2rst & \text{if} \quad r < s \\ r^2 + s^2 - 2srt & \text{if} \quad r > s \end{cases} = s^2 + r^2 - 2rst$$

The integral over t can be computed explicitly. A short computation shows

$$\int_{-1}^{1} \frac{1}{\sqrt{1+u^2-2ut}}\, dt = \int_{|1-u|^2}^{|1+u|^2} \frac{1}{\sqrt{x}}\, dx = 2. \tag{112}$$

Putting everything together we find

$$\phi(re_3) = 4\pi \int_0^\infty \frac{\rho(s)}{\max\{r,s\}}\, s^2 ds = \int_{\mathbb{R}^3} \frac{\rho(|y|)}{\max\{r,|y|\}}\, dy, \tag{113}$$

as well as

$$\int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|}\, dy = \int_{\mathbb{R}^3} \frac{\rho(y)}{\max\{|x|,|y|\}}\, dy. \tag{114}$$

This proves the first equality in (105). The second is a direct consequence of the first. $\blacksquare$

Remark 11: Newton's theorem is particularly useful if ρ has compact support, i.e. $\operatorname{supp}(\rho) = B_R(0)$ for some $R>0$. In this case

$$\int_{\mathbb{R}^3} \frac{1}{|x-y|} \rho(y) \, dy = \frac{1}{|x|} \int_{\mathbb{R}^3} \rho(y) \, dy \qquad (115)$$

holds for $|x|>R$. The physical interpretation of (115) is that the electrostatic potential $\phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|} \rho(y) \, dy$ of any radial charge distribution looks like that of a point charge from far away.

The next lemma is a technical statement that follows from Hardy's inequality. We will sketch the proof of this important inequality after the proof of the lemma.

<u>**Lemma 10:**</u> Let ϱ be a bounded positive Borel measure (i.e. $\varrho(\mathbb{R}^3) < \infty$ and $\varrho(A) \geq 0$ for all Borel measurable sets A) and let $\phi(x) = \int_{\mathbb{R}^3} \frac{1}{|x-y|} d\varrho(y) \geq 0$. Then we have for all real-valued functions $\Psi \in H^2(\mathbb{R}^3)$ and all $\varepsilon > 0$:

$$\int_{\mathbb{R}^3} \frac{\Psi(x)}{\phi(x) + \varepsilon} \left(-\Delta \Psi(x)\right) dx \geq 0. \tag{116}$$

Moreover, there is equality if and only if $\Psi = 0$.

<u>**Proof:**</u> Using a density argument we check that it is sufficient to prove the lemma for a real-valued function $\Psi \in C_c^\infty(\mathbb{R}^3)$ (check!). Let us denote

$\varphi(x) = \dfrac{\Psi(x)}{\phi(x)+\varepsilon}$. We have

$$\int_{\mathbb{R}^3} \frac{\Psi(x)}{\phi(x)+\varepsilon}\left(-\Delta\Psi(x)\right)dx = \int_{\mathbb{R}^3} \nabla\varphi(x)\cdot\nabla\Big(\big(\phi(x)+\varepsilon\big)\,\varphi(x)\Big)dx$$

$$\geq \int_{\mathbb{R}^3} \nabla\varphi(x)\cdot\nabla\big(\phi(x)\varphi(x)\big)\,dx \tag{117}$$

$$\overset{\text{Fubini}}{=} \int_{\mathbb{R}^3}\left(\int_{\mathbb{R}^3} \nabla\varphi(x)\cdot\nabla\left(\frac{1}{|x-y|}\varphi(x)\right)dx\right)d\rho(y),$$

and hence the statement follows if we can show that

$$\int_{\mathbb{R}^3} \nabla f(x)\cdot\nabla\left(\frac{1}{|x|}f(x)\right)dx \geq 0 \tag{118}$$

holds for all real-valued functions $f\in H^2(\mathbb{R}^3)$ (Note that $\varphi\in H^2(\mathbb{R}^3)$.). To that end, we again change variables and define $\chi(x) = \dfrac{\varphi(x)}{|x|^{1/2}}$. We obtain

$$\int_{\mathbb{R}^3} \nabla\varphi(x)\cdot\nabla\left(\frac{\varphi(x)}{|x|}\right)dx = \int_{\mathbb{R}^3} \nabla\left(|x|^{1/2}\chi(x)\right)\cdot\nabla\left(\frac{\chi(x)}{|x|^{1/2}}\right)dx$$

$$= \int_{\mathbb{R}^3}\left(\frac{1}{2}\,\frac{x}{|x|^{3/2}}\chi(x) + |x|^{1/2}\,\nabla\chi(x)\right)\cdot\left(-\frac{1}{2}\,\frac{x}{|x|^{5/2}}\chi(x) + \frac{\nabla\chi(x)}{|x|^{1/2}}\right)dx$$

$$= \int_{\mathbb{R}^3} |\nabla\chi(x)|^2\,dx - \frac{1}{4}\int_{\mathbb{R}^3}\frac{\chi^2(x)}{|x|^2}\,dx \geq 0. \qquad (119)$$

The fact that the r.h.s. of (119) is nonnegative is called **Hardy's inequality**. It is known that the inequality is strict for any χ that is not identically zero. This proves Lemma 10.

$\blacksquare$

Theorem 4 (Hardy's inequality): For $d \geq 3$ and any $\psi \in H^1(\mathbb{R}^d)$ we have

$$\int_{\mathbb{R}^d} |\nabla \psi(x)|^2 dx \geq \frac{(d-2)^2}{4} \int_{\mathbb{R}^3} \frac{|\psi(x)|^2}{|x|^2} dx. \tag{120}$$

The inequality is strict unless $\psi = 0$.

Proof sketch: In order to be not taken to far apart we will only sketch the proof, that is, we ignore some technical details and assume that ψ is sufficiently smooth.

We can write $\psi(x) = |x|^{1-d/2} g(x)$ with g having the property that $g(0) = 0$, for otherwise both sides of (120) will be infinite. We have

$$\nabla \psi(x) = \left(1 - \frac{d}{2}\right) |x|^{-d/2} \frac{x}{|x|} g(x) + |x|^{1-d/2} (\nabla g)(x), \tag{121}$$

and hence

$$|\nabla \Psi(x)|^2 = \underbrace{\left(1-\frac{d}{2}\right)^2}_{\frac{(d-2)^2}{4}} \underbrace{|x|^{-d}\,|g(x)|^2}_{\frac{|\Psi(x)|^2}{|x|^2}} + |x|^{2-d}\,|\nabla g(x)|^2$$

partial derivative in radial direction

$$+ (2-d)\,\mathrm{Re}\,|x|^{1-d}\,\overline{g(x)}\,\underbrace{\nabla g(x)\cdot\frac{x}{|x|}}_{=\partial_r g(x)} \qquad (122)$$

The last term vanishes after integration over x, since

$$\int_{\mathbb{R}^d} |x|^{1-d}\,\mathrm{Re}\,\overline{g(x)}\,\partial_r g(x)\,dx \underset{\text{go to spherical coordinates}}{=} \frac{1}{2}\int_{S^{d-1}_r}\int_0^\infty \partial_r\,|\underbrace{\tilde{g}(r,\omega)}_{=g(x(r,\omega))}|^2\,dr\,d\omega \qquad (133)$$

$= 0$ because g has compact support (integration over r for fixed ω equals 0).

The second term on the r.h.s. of (122) is strictly positive, and hence

$$\int_{\mathbb{R}^3} |\nabla\Psi(x)|^2\,dx \geq \frac{(d-2)^2}{4}\int_{\mathbb{R}^3} \frac{|\Psi(x)|^2}{|x|^2}\,dx. \qquad (134)$$

Using that we dropped the second term on the r.h.s. of (122) we can also see that the inequality is strict unless $\psi = 0$.

$\blacksquare$

Remark 12: The constant $\frac{(d-2)^2}{4}$ in (120) is **sharp** in the sense that the inequality with a larger constant is wrong for some ψ.

Remark 13: Please recall Remark 5.3.2 in Section 5 on the Schrödinger equation. The above theorem and the previous remark imply that the energy $(\kappa \geq 0)$

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^d} |\nabla \psi(x)|^2 dx - \kappa \int_{\mathbb{R}^d} \frac{|\psi(x)|^2}{|x|^2} dx \qquad (135)$$

is bounded from below if $\kappa \leq \frac{(d-2)^2}{4}$. (This does not follow from Theorem 5.3.1.)

After this longer but very interesting excursion, we are now prepared to give the proof of Theorem 2.

Proof of Theorem 2: In the first step we show that $J^V(\varepsilon) < 0$ for $\varepsilon > 0$ small enough. In combination with $J^V(0) = 0$ and Proposition 1 this proves $\lambda_c > 0$. To establish $J^V(\varepsilon) < 0$ we first show the existence of a function $\phi \in H^1(\mathbb{R}^3)$ with

$$\frac{1}{2}\int_{\mathbb{R}^3} |\nabla\phi(x)|^2 dx + \int_{\mathbb{R}^3} V(x)\,|\phi(x)|^2 dx < 0. \qquad (136)$$

In Exercise 3b on sheet no. 7 we saw that

$$\Psi_z(x) = \sqrt{\frac{z_1^3}{\pi}}\ \exp\left(-z|x|\right), \quad \underset{z_1>0}{x \in \mathbb{R}^3} \qquad (137)$$

solves the equation

$$-\frac{1}{2}\Delta\Psi_z(x) - \frac{z}{|x|}\Psi_z(x) = e(z)\Psi(x) \qquad (138)$$

with $e(z) = -\frac{z^2}{2}$. We also denote $\tilde{\Psi}(x) = \Psi_{z_1}(x-R_1)$ with z_1 and R_1 in (107). Using $\tilde{\Psi}$ as a test function we find

$$\underbrace{\frac{1}{2}\int_{\mathbb{R}^3}|\nabla\tilde{\Psi}(x)|^2\,dx - \sum_{m=1}^{M} z_m \int_{\mathbb{R}^3} \frac{1}{|x-R_m|}|\tilde{\Psi}(x)|^2\,dx}_{\geq 0}$$

$$\leq \frac{1}{2}\int_{\mathbb{R}^3}|\nabla\tilde{\Psi}(x)|^2\,dx - \int_{\mathbb{R}^3}\frac{z_1}{|x-R_1|}|\tilde{\Psi}(x)|^2\,dx = e(z_1). \qquad (139)$$

We use $\sqrt{\varepsilon}\,\tilde{\Psi} \in S(\varepsilon)$ as a test function for $\mathcal{E}^V(v)$ and (139) to see that

$$J^V(\varepsilon) \leq \mathcal{E}^V(\sqrt{\varepsilon}\,\tilde{\Psi}) \leq \varepsilon\, e(z_1) + O(\varepsilon^{10/3}). \qquad (140)$$

please check

Since $e(z_1) < 0$ this proves $J^V(\varepsilon) < 0$ for $\varepsilon > 0$ small enough.
We conclude that $\lambda_c > 0$.

In the next step we show that $\lambda_c \geq Z$. We may assume w.l.o.g. that $\lambda_c < \infty$ because otherwise there is nothing to prove. Hence, there exists a minimizer ϕ_{λ_c} for the variational problem $J^V(\lambda_c)$. Since $\lambda_c > 0$ we can apply Proposition 2 and deduce that ϕ_{λ_c} is the eigenfunction of the operator $H_{\phi_{\lambda_c}}$ (for a definition see the proposition) corresponding to its lowest eigenvalue $\mu_{\lambda_c} = 0$ (by Lemma 8). To prove $\lambda_c \geq Z$ we will argue by contradiction and show that $\lambda_c < Z$ implies that the lowest eigenvalue of H_{λ_c} is negative (this contradicts $\mu_{\lambda_c} = 0$). To that end, we will construct a test function $\chi_R \in H^1(\mathbb{R}^3)$ with the property that $\mu_{\lambda_c} < Z$ implies

$$\underbrace{\langle \chi_R, H_{\lambda_c}\chi_R\rangle} < 0. \tag{141}$$

This expression needs to be understood in the sense that one integrates by parts to write $\langle \chi_R, -\Delta \chi_R\rangle$ as $\int_{\mathbb{R}^3} |\nabla \chi_R(x)|^2 dx$.

Since $\mu_{\lambda_c} = \inf_{\substack{\phi\in H^1(\mathbb{R}^3)\\ \|\phi\|_2=1}} \langle \phi, H_{\lambda_c}\phi\rangle$, this shows that the lowest eigenvalue of H_{λ_c} is negative and yields the desired contradiction.

We start by defining the function χ_R. Let χ be a smooth real, radial function with support in the annulus $\{1 \le |x| \le 2\}$ with $\int_{\mathbb{R}^3} |\chi(x)|^2 dx = 1$. The function χ_R is defined by $\chi_R(x) = R^{-3/2}\chi(x/R)$ for $R>0$, which has support in the annulus $\{R \le |x| \le 2R\}$ and satisfies $\|\chi_R\|_2 = 1$.

The choice of χ_R is motivated by the following observation. To get a negative energy it is natural to make the kinetic energy very small, which can be achieved with functions that are very much spread out in space. If such a function lives on the length scale $R \gg 1$, then the kinetic energy scales as R^{-2}. This is much smaller than the Coulomb energy, which, as we will see below, behaves as a negative constant that depends on $Z - \lambda_c$ times R^{-1}. To be able to control the other potential terms, we have to put our test function far away from the origin and use the decay of the potentials.

We recall that

$$H_{\phi_{\lambda_c}} = -\frac{\Delta}{2} + V + C_{TF}\,|\phi_{\lambda_c}|^{4/3} + |\phi_{\lambda_c}|^2 * \frac{1}{|x|}, \tag{142}$$

that is, we need to consider

$$\langle \chi_R, H_{\phi_{\lambda_c}} \chi_R \rangle = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \chi_R(x)|^2 dx + \int_{\mathbb{R}^3} V(x) \, |\chi_R(x)|^2 dx$$

$$+ \, C_{TF} \int_{\mathbb{R}^3} |\phi_{\lambda_c}(x)|^{4/3} \, |\chi_R(x)|^2 \, dx$$

$$+ \int |\phi_{\lambda_c}|^2 * \frac{1}{|\cdot|}(x) \, |\chi_R(x)|^2 dx. \qquad (143)$$

To have a shorter notation at hand, we define $W(x) = C_{TF} |\phi_{\lambda_c}(x)|^{4/3}$ as well as the measure

δ-measure with unit mass at R_m

$$d\varrho(x) = |\phi_{\lambda_c}(x)|^2 dx - \sum_{m=1}^{M} z_m \, \delta_{R_m}(x), \qquad (144)$$

which allows us to write the above energy as

$$\langle \chi_R, H_{\phi_{\lambda_c}} \chi_R \rangle = \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \chi_R(x)|^2 dx + \int_{\mathbb{R}^3} W(x) \, |\chi_R(x)|^2 dx$$

$$+ \int_{\mathbb{R}^3} \varrho * \frac{1}{|\cdot|}(x) \, |\chi_R(x)|^2 dx. \qquad (145)$$

An application of Newton's theorem shows

$$\int_{\mathbb{R}^3} \frac{|\chi_R(y)|^2}{|x-y|}\,dy = \int_{|y|\geq R} \frac{|\chi_R(y)|^2}{|y|}\,dy = \frac{1}{R}\int_{\mathbb{R}^3} \frac{|\chi(x)|^2}{|y|}\,dy$$

if $|x| \leq R$ and

$$\int_{\mathbb{R}^3} \frac{|\chi_R(y)|^2}{|x-y|}\,dy = \underbrace{\frac{1}{|x|}}_{\underset{|x|>R}{\leq}\ \frac{1}{R}} \int_{|y|\leq|x|} |\chi_R(y)|^2\,dy + \underbrace{\int_{|y|>|x|} \frac{|\chi_R(y)|^2}{|y|}\,dy}_{\underset{|x|>R}{\leq}\ \frac{1}{R}\int |\chi_R(y)|^2\,dy}$$

$$\overset{|x|>R}{\leq} \frac{1}{R}\int_{\mathbb{R}^3} |\chi_R(y)|^2\,dy = \frac{1}{R} \tag{146}$$

if $|x| > R$. Using this, we obtain the following bound

$$\left\langle \chi_R, \left(\rho * \frac{1}{|\cdot|}\right)\chi_R \right\rangle = \int_{\mathbb{R}^3} \left(\chi_R^2 * \frac{1}{|\cdot|}\right)(x)\, d\rho(x)$$

$$= \rho\big(B_R(0)\big)\ \frac{1}{R} \int_{\mathbb{R}^3} \frac{|\chi(y)|^2}{|y|}\,dy + \int_{|x|\geq R} \left(\chi_R^2 * \frac{1}{|\cdot|}\right)(x)\,d\rho(x)$$

ball with radius R
centered around 0

$$\leq \frac{\rho(B_R(0))}{R} \int_{\mathbb{R}^3} \frac{|\chi(y)|^2}{|y|}\,dy + \frac{\rho_+\big(B_R^c(0)\big)}{R} \tag{147}$$

$$\leq \frac{\rho(\mathbb{R}^3)}{R} \int_{\mathbb{R}^3} \frac{|\chi(y)|^2}{|y|}\,dy + \frac{|\rho|\big(B_R^c(0)\big)}{R},$$

where $B_R^c(0) = \mathbb{R}^3 \setminus B_R(0)$ and $|\rho|$ is the absolute value of the signed measure $\rho = \underbrace{\rho_+}_{\geq 0} - \underbrace{\rho_-}_{\geq 0}$, i.e., $|\rho| = \rho_+ + \rho_-$.

[Every signed measure ρ can be written as $\rho = \rho_+ - \rho_-$ with two positive measure with disjoint support ρ_+ and ρ_-.]

To come to the last line we used

$$\rho\big(B_R(0)\big) = \rho(\mathbb{R}^3) - \rho\big(B_R^c(0)\big) \leq \rho(\mathbb{R}^3) + \rho_-\big(B_R^c(0)\big) \tag{148}$$

as well as

$$\int_{\mathbb{R}^3} \frac{\chi^2(y)}{|y|}\, dy \leq 1 \,, \tag{149}$$

which follows because the support of χ lies outside the ball with radius 1. We note that dominated convergence implies

$$\lim_{R\to\infty} |\varrho|\left(B_R^c(0) \right) = 0 . \tag{150}$$

Next, we derive a bound for the term involving ω:

$$\langle \chi_R, \omega \chi_R \rangle = \int_{|x|\geq R} \omega(x)\, \chi_R^2(x)\, dx \tag{151}$$

$$1 = \frac{1}{p} + \frac{1}{q} \quad \overset{\text{Hölder}}{\leq} \left(\int_{|x|\geq R} |\omega(x)|^p \, dx \right)^{1/p} \left(\int_{|x|\geq R} |\chi_R(x)|^{2q} \, dx \right)^{1/q}$$

$$= \frac{1}{R^{3/p}} \left(\int_{|x|\geq R} |\omega(x)|^p dx \right)^{1/p} \left(\int_{\mathbb{R}^3} |\chi(x)|^{2q} \, dx \right)^{1/q} .$$

Finally, the kinetic energy of χ_R reads

$$\frac{1}{2}\int_{\mathbb{R}^3} |\nabla\chi_R(x)|^2 dx = \frac{1}{2R^2}\int_{\mathbb{R}^3} |\nabla\chi(x)|^2 dx. \tag{152}$$

In combination, these three bounds show

$$\langle \chi_R, H_{\Phi_{\lambda_c}} \chi_R \rangle \leq \frac{\varrho(\mathbb{R}^3)}{R}\int_{\mathbb{R}^3} \frac{\chi^2(y)}{|y|} dy + \frac{|\varrho|\left(B_R^c(0)\right)}{R}$$

$$+ \frac{1}{2R^2}\int_{\mathbb{R}^3} |\nabla\chi(x)|^2 dx + \frac{1}{R^{\frac{3}{p}}}\left(\int_{|x|\geq R} |w(x)|^p\, dx\right)^{\frac{1}{p}} \|\chi\|^2_{L^{2q}(\mathbb{R}^3)}. \tag{153}$$

Let us have a closer look at this expression. We have

$$\varrho(\mathbb{R}^3) = \underbrace{\int_{\mathbb{R}^3} |\Phi_{\lambda_c}(x)|^2 dx}_{=\lambda_c} - \sum_{m=1}^{M} z_m \underbrace{\delta_{R_m}(\mathbb{R}^3)}_{=1}$$

$$= \lambda_c - Z \underset{\text{by assumption}}{<} 0. \tag{154}$$

We insert $\omega(x) = C_{TF} |\phi_{\lambda_c}(x)|^{4/3}$ in the last term in (153), choose $p = \frac{3}{2}$ ($\Rightarrow q = 3$) and find

$$\left(\int_{|x| \geq R} |\omega(x)|^p \, dx \right)^{\frac{1}{p}} \leq C_{TF} \Bigg(\underbrace{\int_{\mathbb{R}^3} |\phi_{\lambda_c}(x)|^2 \, dx}_{\lambda_c} \Bigg)^{2/3},$$

$$\|\chi\|^2_{L^{2q}(\mathbb{R}^3)} = \|\chi\|^2_{L^6(\mathbb{R}^3)} . \tag{155}$$

Hence,

$$\langle \chi_R , H_{\phi_{\lambda_c}} \chi_R \rangle \leq \frac{(\lambda_c - Z)}{R} \int_{\mathbb{R}^3} \frac{\chi^2(y)}{|y|} dy + \frac{|\varrho|(B_R^c(0))}{R}$$

$$+ \frac{1}{2R^2} \int_{\mathbb{R}^3} |\nabla \chi(x)|^2 dx + \frac{\text{const.}}{R^2} \|\chi\|^2_{L^6(\mathbb{R}^3)} . \tag{156}$$

Using (150) and $(\lambda_c - Z) < 0$, we check that (156) implies $\langle \chi_R , H_{\phi_{\lambda_c}} \chi_R \rangle < 0$ for R large enough. This yields the desired contradiction and we conclude that $\lambda_c \geq Z$.

It remains to show that $\lambda_c \leq 2Z$. Let λ be s.t. $\mathcal{J}^V(\lambda)$ has a minimizer and denote by ϕ_λ the unique positive minimizer. We know that

$$\left(-\frac{\Delta}{2} + V(x) + C_{TF}\,|\phi_\lambda(x)|^{4/3} + |\phi_\lambda|^2 * \frac{1}{|\cdot|}(x)\right)\phi_\lambda = \mu\phi_\lambda \qquad (157)$$

with $\lambda \leq 0$. Let us multiply this equation by $\phi_\lambda(x)\,\frac{1}{-U(x)+\varepsilon}$ and integrate over $\mathbb{R}^3$. We find

$$\underbrace{\frac{1}{2}\int_{\mathbb{R}^3} \frac{\phi_\lambda(x)}{-U(x)+\varepsilon}\left(-\Delta\phi_\lambda(x)\right)dx}_{\substack{\geq 0 \\ \uparrow \\ \text{Lemma } 10}} + \int_{\mathbb{R}^3} \frac{\phi_\lambda^2(x)}{-U(x)+\varepsilon}\left(V(x) + C_{TF}\,|\phi_\lambda(x)|^{4/3}\right)dx$$

$$+ \int_{\mathbb{R}^6} \frac{\phi_\lambda^2(x)\,\phi_\lambda^2(y)}{|x-y|\,(-U(x)+\varepsilon)}\,d(x,y) = \mu \leq 0 \qquad (158)$$

and conclude that

$$\int_{\mathbb{R}^3} \frac{\phi_\lambda^2(x)\,U(x)}{-U(x)+\varepsilon}\,dx + \int_{\mathbb{R}^6} \frac{\phi_\lambda^2(x)\,\phi_\lambda^2(y)}{|x-y|\,(-U(x)+\varepsilon)}\,d(x,y) \leq 0. \qquad (159)$$

We also note that

$$\int_{\mathbb{R}^6} \frac{\phi_\lambda^2(x)\,\phi_\lambda^2(y)}{(-U(x)+\varepsilon)\,|x-y|}\, d(x,y) = \int_{\mathbb{R}^6} \frac{\phi_\lambda^2(x)\,\phi_\lambda^2(y)}{(-U(y)+\varepsilon)\,|x-y|}\, d(x,y)$$

$$= \frac{1}{2}\int_{\mathbb{R}^6} \left(\frac{1}{-U(x)+\varepsilon} + \frac{1}{-U(y)+\varepsilon}\right) \frac{\phi_\lambda^2(x)\,\phi_\lambda^2(y)}{|x-y|}\, d(x,y)$$

$$\geq \frac{1}{2}\int_{\mathbb{R}^6} \frac{\big(-U(x)-U(y)\big)}{|x-y|}\,\frac{\phi_\lambda^2(x)\,\phi_\lambda^2(y)}{(-U(x)+\varepsilon)(-U(y)+\varepsilon)}\, d(x,y) \tag{160}$$

$$\left[\begin{array}{l} x,y \geq 0 \\ \varepsilon > 0 \end{array} \Rightarrow \frac{1}{x+\varepsilon} + \frac{1}{y+\varepsilon} = \frac{x+y+2\varepsilon}{(x+\varepsilon)(y+\varepsilon)} \geq \frac{x+y}{(x+\varepsilon)(y+\varepsilon)}\right]$$

as well as that $|x+R| + |y+R| \geq |x-y|$ (triangle ineq.) implies

$$\frac{-U(x)-U(y)}{|x-y|} = \sum_{m=1}^{M} Z_m \left(\frac{1}{|x-R_m|} + \frac{1}{|y-R_m|}\right)\frac{1}{|x-y|}$$

$$\geq \sum_{m=1}^{M} \frac{Z_m}{|x-R_m|\,|y-R_m|}\,. \tag{161}$$

Using these two bounds, we deduce that

$$\int_{\mathbb{R}^6} \frac{\phi_\lambda^2(x)\phi_\lambda^2(y)}{(-U(x)+\varepsilon)|x-y|}\, d(x,y) \geq \frac{1}{2}\sum_{m=1}^{M} z_m \left(\int_{\mathbb{R}^3} \frac{\phi_\lambda^2(x)}{|x-R_m|(-U(x)+\varepsilon)}\, dx \right)^2$$

$$\geq \frac{Z}{2} \left(\sum_{m=1}^{M} \frac{z_m}{Z} \int_{\mathbb{R}^3} \frac{\phi_\lambda^2(x)}{|x-R_m|(-U(x)+\varepsilon)}\, dx \right)^2$$

convexity of $x \mapsto x^2$

$$= \frac{1}{2Z} \left(\int_{\mathbb{R}^3} \frac{-U(x)}{-U(x)+\varepsilon}\, \phi_\lambda^2(x)\, dx \right)^2. \qquad (162)$$

When we insert this bound into (159) we find

$$0 \geq -\int_{\mathbb{R}^3} \frac{-U(x)}{-U(x)+\varepsilon}\, \phi_\lambda^2(x)\, dx + \frac{1}{2Z} \left(\int_{\mathbb{R}^3} \frac{-U(x)}{-U(x)+\varepsilon}\, \phi_\lambda^2(x)\, dx \right)^2$$

$$\left[(x>0) : \frac{1}{2Z}x^2 - x \leq 0 \iff \frac{1}{2Z}x^2 \leq x \iff x \leq 2Z \right]$$

$$\Rightarrow \int_{\mathbb{R}^3} \frac{-U(x)}{-U(x)+\varepsilon}\, \phi_\lambda^2(x)\, dx \leq 2Z. \qquad (163)$$

Passing to the limit $\varepsilon \to 0$ (please check that this is possible), we obtain

$$\lambda = \int_{\mathbb{R}^3} \Phi_\lambda^2(x)\, dx \leq 2Z. \tag{164}$$

This inequality holds whenever λ is s.t. $J^V(\lambda)$ has a minimizer, in particular for $\lambda = \lambda_c$. This proves Theorem 2.

$\blacksquare$

5. Regularity and decay of ϕ_λ

In this section we discuss the regularity of the unique minimizer of $J^V(\lambda)$ for $\lambda \in [0, \lambda_c]$ and its decay properties. The first statement we are going to discuss is the following theorem.

Theorem 5 (Regularity): Let ϕ be the unique positive minimizer for $J^V(\lambda)$ with $\lambda \leq \lambda_c$. Then $\phi \in C^0(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{R_m\}_{m=1}^M)$. The function $\nabla\phi$ is not continuous at $R_1, \dots, R_M$: The following Kato's cusp property holds for every $m = 1 \dots M$:

$$z_m \phi(R_m) = \lim_{r \to 0} \int_{S^2} n \cdot \nabla\phi(R_m + rn)\, d\omega(n), \qquad (165)$$

where S^2 is the sphere of radius 1 in $\mathbb{R}^3$ and $d\omega$ is the uniform probability measure on S^2.

Remark 14: If $\nabla\phi$ were continuous, we would have

$$\lim_{r\to 0} \int_{S^2} u \cdot \nabla\phi(R_m + ru)\, d\omega(u) = \left(\int_{S^2} u\, d\omega(u) \right) \cdot \nabla\phi(R_m) = 0. \quad (166)$$

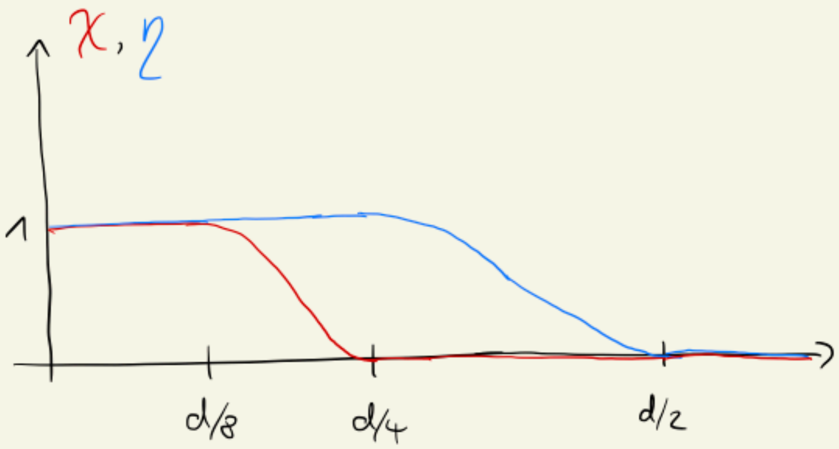
Since $\phi(R_m) > 0$ this proves that $\nabla\phi$ cannot be continuous.

Remark 15: The regularity of ϕ should be compared to that of the ground state wave function of the Hamiltonian of the hydrogen atom, see exercise 3b on sheet no. 7.

Proof of Theorem 5: The fact that ϕ is continuous on $\mathbb{R}^3$ is a consequence of the Sobolev embedding $H^2(\mathbb{R}^3) \hookrightarrow C_0^0(\mathbb{R}^3)$. In the following we use the notation $h(x) = |\phi|^2 * \frac{1}{|\cdot|}(x)$. The Euler-Lagrange equation $\mathcal{E}^U$ in (75) can be written as

$$\begin{cases} -\frac{\Delta}{2}\phi(x) + V(x)\phi(x) + W(x)\phi(x) + C_{TF}\,\phi^{7/3}(x) = \mu\phi(x) \\ -\Delta W(x) = 4\pi\,\phi^2(x). \end{cases} \qquad (167)$$

Let $x_0 \in \mathbb{R}^3 \setminus \{R_m\}_{m=1}^{M}$ and $d = \min_{0\le m\le M} |x_0 - R_m| > 0$. We fix two smooth functions χ and η s.t. $\chi|_{B_{d/8}(x_0)} \equiv 1$, $\chi|_{B^c_{d/4}(x_0)} \equiv 0$, $\eta|_{B_{d/4}(x_0)} \equiv 1$ and $\eta|_{B^c_{d/2}(x_0)} \equiv 0$.



Using (167) and $\eta\chi = \chi$, hence that $W(\chi\phi) = (\eta W)(\chi\phi)$, we obtain

$$\Delta(\chi\phi) = 2V\chi\phi + 2(\eta W)(\chi\phi) + 2C_{TF}\,|\phi|^{4/3}\phi - 2\mu\chi\phi + 2\nabla\chi\cdot\nabla\phi + \phi(\Delta\chi) \qquad (168)$$

as well as

$$\Delta(\eta W) = -4\pi\eta\phi^2 + 2\nabla\eta\cdot\nabla W + W(\Delta\eta). \tag{169}$$

When we differentiate once more, we get that $\chi\phi, \eta W \in H^3(\mathbb{R}^3)$, hence $\phi, W \in H^3_{loc}(\mathbb{R}^3 \setminus \{R_m\}_{m=1}^{M})$. Iterating the above argument leads to $\phi, W \in H^k_{loc}(\mathbb{R}^3 \setminus \{R_m\}_{m=1}^{M})$ for all $k \geq 1$. Using Sobolev embeddings (see Wikipedia or a PDE book for embeddings of Sobolev spaces into spaces of continuous functions), we conclude that $\phi, W \in C^\infty(\mathbb{R}^3 \setminus \{R_m\}_{m=1}^{M})$.

Next, we prove (165) by integrating the Euler-Lagrange equation of $\mathcal{E}^V$ in (75) over a small ball $B_r(R_m)$:

$$\int_{B_r(R_m)} \Delta\phi(x)\,dx = 2z_m \int_{B_r(R_m)} \frac{\phi(x)}{|x-R_m|}\,dx + 2\sum_{k\neq m} z_k \int_{B_r(R_m)} \frac{\phi(x)}{|x-R_k|}\,dx$$

$$+ 2c_{TF}\int_{B_r(R_m)} \phi^{7/3}(x)\,dx + 2\int_{B_r(R_m)} W(x)\phi(x)\,dx - 2\mu\int_{B_r(R_m)} \phi(x)\,dx. \tag{170}$$

We have

$$\int_{B_r(R_m)} \Delta\phi(x)\, dx \underset{\substack{\uparrow \\ \text{Gauß theorem}}}{=} \int_{\partial B_r(R_m)} n\cdot\nabla\phi(x)\, dx = 4\pi r^2 \int_{S^2} n\cdot\nabla\phi(R_m + rn)\, d\omega(n), \tag{171}$$

which implies

$$\lim_{r\to 0} \int_{S^2} n\cdot\nabla\phi(R_m+rn)\, d\omega(n) = \lim_{r\to 0} \frac{1}{4\pi r^2}\Big(\text{terms on the r.h.s. of (170)}\Big). \tag{172}$$

For all except for the first term on the r.h.s. of (170) the r.h.s. of (172) vanishes as $r\to 0$. For the first term we have

$$\lim_{r\to 0} \frac{1}{r^2}\int_{B_r(R_m)} \frac{\phi(x)}{|x-R_m|}\, dx \underset{\substack{\uparrow \\ \text{use spherical} \\ \text{coordinates with center } R_m}}{=} \lim_{r\to\infty} \frac{1}{r^2}\int_0^r\int_{S^2} \frac{\phi(sn+R_m)}{\underbrace{|sn|}_{=s}}\, s^2\, ds\, d\omega(n)$$

$$= \lim_{r\to\infty} \frac{1}{r^2}\int_0^r \left(\int_{S^2} \phi(sn+R_m)\, d\omega(n)\right) s\, ds$$

$$= \frac{1}{2} \int_{S^2} \phi(R_m)\, d\omega(u) = 2\pi\, \phi(R_m). \tag{173}$$

Hence,

$$\lim_{r \to 0} \int_{S^2} u \cdot \nabla\phi(R_m + ru)\, d\omega(u) = Z_m \phi(R_m), \tag{174}$$

which proves the claim. $\blacksquare$

The last property of the minimizer of the TFW functional we discuss is its decay. We have the following statement.

Theorem 6 (Exponential decay): Let ϕ_λ be the unique minimizer for $J^V(\lambda)$, with $\lambda < \lambda_c$ and $\mu_\lambda < 0$ the associated Lagrange multiplier in (75). Then for every

$0 < \varepsilon < -\mu_\lambda$, there exists a constant C_ε s.t.

$$|\phi_\lambda(x)| \leq C_\varepsilon \exp\left(-\sqrt{-2(\mu_\lambda+\varepsilon)}\,|x|\right). \tag{175}$$

It also holds that

$$\int_{|x|>R} |\phi_\lambda(x)|^2 dx + \int_{|x|\geq R} |\nabla\phi_\lambda(x)|^2 dx \leq C_\varepsilon \exp\left(-2\sqrt{-2(\mu_\lambda+\varepsilon)}\,R\right). \tag{176}$$

Proof: Let $0 < \varepsilon < -\mu_\lambda$ and let us denote by ϕ_λ the unique positive minimizer of $J^V(\lambda)$. Using (75) we see that

$$\left(-\Delta + 2(\mu_\lambda+\varepsilon)\right)\phi_\lambda = 2\left(-\varepsilon - V - |\phi_\lambda|^2 * \frac{1}{|\cdot|} - C_{TF}\,|\phi_\lambda|^{4/3}\right)\phi_\lambda$$

$$=: g. \tag{177}$$

Since $\phi_\lambda \in H^2(\mathbb{R}^3)$ we know that $g \in L^2(\mathbb{R}^3)$. An application of Lemma 5.5.1 in Section 5, see also Remark 5.5.2, shows

$$\Phi_\lambda(x) = \frac{1}{4\pi} \int_{\mathbb{R}^3} \frac{\exp\left(-\sqrt{-2(\mu_\lambda+\varepsilon)}\,|x-y|\right)}{|x-y|} g(y)\,dy. \qquad (178)$$

Next, we claim that $g(x) < 0$ for $|x| \geq R_\varepsilon$ with R_ε chosen large enough. In fact, the only positive term on the r.h.s. of (177) is $-V(x)\Phi_\lambda(x)$ and we have $-V(x) \leq \varepsilon/2$ for $x \in B_{R_\varepsilon}(0)$ with R_ε chosen large enough. Accordingly,

$$\Phi_\lambda(x) \leq \frac{1}{4\pi} \int_{|y| \leq R_\varepsilon} \frac{\exp\left(-\sqrt{-2(\mu_\lambda+\varepsilon)}\,|x-y|\right)}{|x-y|} g(y)\,dy \qquad (179)$$

as well as for $|x| > 2R_\varepsilon$

$$\Phi_\lambda(x) \leq C_\varepsilon \exp\left(-\sqrt{-2(\mu_\lambda+\varepsilon)}\,|x|\right). \qquad (180)$$

The estimate for Φ_λ in (175) follows when we combine (180) and the fact that Φ_λ is bounded in $B_{2R_\varepsilon}(0)$, which follows by Sobolev embedding because $\Phi_\lambda \in H^2(\mathbb{R}^3) \subset L^\infty(\mathbb{R}^3)$.

The estimate on $\int_{|x|\geq R} |\phi_\lambda(x)|^2 dx$ in (176) is a simple consequence of (175) applied for $\varepsilon/2$ instead of ε.

To obtain the bound for $\int_{|x|\geq R} |\nabla\phi_\lambda(x)|^2 dx$ in (176) we multiply (177) by $\chi\phi_\lambda$, where χ is a smooth function with $\chi\big|_{B_R^c(0)} \equiv 1$ and $\chi\big|_{B_{R-1}(0)} \equiv 0$. Integrating by parts and using the decay in $L^2(\mathbb{R}^3)$ easily leads to the stated result.

$\blacksquare$

Remark 16: One can actually show that $\lambda_c > Z$. Using this fact it is possible to prove that ϕ_λ also decays fast for $\lambda = \lambda_c$.

6. Summary

Let us summarize the essential features of the Thomas-Fermi-von Weisäcker functional $\mathcal{E}^V$.

- The TFW functional $\mathcal{E}^V$ is w.l.s.c. on $H^1(\mathbb{R}^3)$. Intuitively this means that any sequence escaping to infinity must carry a nonnegative amount of energy. W.l.s.c. implies that all minimizing sequences for $J^V(\lambda)$ are precompact when the binding inequalities $J^V(\lambda) < J^V(\lambda')$ hold for all $0 \le \lambda' < \lambda$.

- The second main feature of $\mathcal{E}^V$ is its convexity w.r.t. the density $\rho(x) = |\phi(x)|^2$, which allowed us to define the maximal number λ_c of electrons that the potential V can bind, i.e. the largest λ for which the binding inequality holds. The functional $\mathcal{E}^V$ has a minimizer in the set $S(\lambda)$ for $0 \le \lambda \le \lambda_c$ and no minimizer for $\lambda > \lambda_c$. Another consequence of convexity is the uniqueness of the minimizer up to a complex number with absolute value one.

For our potentials that are used to describe atoms and molecules we have shown that $Z \le \lambda_c \le 2Z$, where Z denotes the sum of the nuclear charges (with a little more effort one can show that $Z < \lambda_c < 2Z$). This proves the stability of neutral and positively charged systems. In this case the density of the minimizer decays exponentially far away from the nuclear charges and it is smooth away from the nuclei. At location of the nuclei it is singular.